Introduction

Porous materials are widely used in everyday life, whether one is aware of them or not. The silica gel as a dehumidifying agent and the activated carbon as a deodorant are traditional porous materials. Another example is traditional Japanese houses, which are made of wood, earth, and paper. Such architecture resulted from long years of innovation through insights that these materials would function to insulate and adjust humidity in Japanese climate, whose temperature and humidity vary over broad ranges. It is amazing how people unconsciously worked out the use of materials with various pore sizes. Tightly sealed modern housing holds in humidity, which has created problems such as molds and bacteria, and there are also concerns about the many illnesses that could result from these. This has focused attention on building materials that incorporate porous materials, and many such materials are being developed. [1, 2] As this shows, porous materials are closely integrated into our lives. Here we shall attempt to classify the porous materials reported to date while taking their function expression mechanisms, and then, based on that classification, describe the synthesis and fabrication methods for some representative porous materials.

Functions and Classification of Porous Materials

Typical porous ceramics and the range of their pore sizes are shown in Fig. 1. [3] There are currently many porous materials with pore sizes from about 0.1 nm to 10 mm. When considering these function expression mechanisms of these materials, the level at which we see pores is important. The function expression of Angstrom-order pores is likely related to interaction with ions, atoms, and molecules, while those in micrometer and millimeter ranges are probably related to adhesion of solid particles on filter. It is assumed that pores size in the middle of this range are related to molecular aggregates and condensed liquids.

In this session, the relationship between pore size and function expression mechanisms is reviewed. Fig. 2 shows the mechanisms of porous materials in relation to gas permeation. [4] When pore size is 10 µm or larger, the mechanism can be regarded as the flow passing through an equivalent packed bed, and for that reason the relationship between a porous material and function can be forecast from the Darcy equation and other relational equations for flow velocity and pressure loss. Molecular diffusion controls the
permeation mechanism of porous materials whose pore sizes are in the approximate range of 0.1 to 10 µm. When pore size and molecular mean free path fall below that range, they are governed by Knudsen diffusion. Permeation flow velocity then is proportional to molecular weight to the 0.5 power. At smaller pore sizes below several nm, an activation process caused by interaction between pore wall surfaces and molecules contributes to the permeation phenomenon, which is called “activation diffusion” or “surface flow.” This is a pore size range in which capillary condensation governs when the gas is a condensing gas such as water vapor. At still smaller pore sizes, permeation selectivity is expressed due to difference in molecule sizes, and one can expect the so-called “molecular sieve effect.” From these examples, the correspondence between pore size and function is apparent. It is in fact clear that properties including porosity, pore shape, interpore networks, pore opening, and pore closing contribute to various function expressions. Table 1 presents the relationship between these pore properties and functions. [5] These are sufficient for considering rough design guidelines of porous materials, but owing to the complex connections between function expression and pore properties such as pore size, porosity, and pore

| micropore | mesopore | macropore |
|-----------|----------|-----------|
| zeolite   | FSM-16, M41S | sol-gel method (colloidal process) |
| sol-gel method (cat. NH₃) | sol-gel method (cat. HCl₃) | phase separation glass |
| sintered powder | honeycomb ceramics | auto filter |
| humidity sensor | enzyme carrier | microbe carrier |
| filter | | |

Fig. 1 Pore size of typical porous ceramics.

Fig. 2 Permeation model of gas in porous materials (modified from Matsukata [4]).
shape, or between function expression and material properties, a method of cataloging them more carefully is desirable from the standpoint of material design.

One method of classifying pores is the International Union of Pure and Applied Chemistry (IUPAC) method, which is internationally recognized. [6] It is based on the Russel classification, in which pores are classified mainly according to the results of nitrogen adsorption experiments. [7, 8] One should be well aware that classification is based on nitrogen adsorption, meaning that the relative sizes of nitrogen molecules and pores must be taken into account. With molecules larger than nitrogen, adsorption resembling micropore filling will occur in the mesopore range. Additionally, caution is needed when working with molecules smaller than nitrogen molecules, such as hydrogen and water. For example, even if materials are non-porous to nitrogen molecules, it is often the case that they are not necessarily non-porous to these smaller molecules. Therefore we think that an index such as the relative pore sizes shown in Table 2 is needed in pore classification. However nitrogen molecules are quadrupole interactive, generally in nitrogen adsorption they can be seen as often forming a multilayer structure as in BET theory, but comparable phenomena do not necessarily occur with other molecules. Thus at this time classification by the presence of molecules in pores is perhaps a practical method.

Based on the foregoing, and using the IUPAC classification as the standard, Table 2 presents the classification based on the function expression discussed above and the phenomena occurring in pores, as well as the pore classification organized by considering the synthesis methods for existing porous materials, discussed below.

| Pore radius range | Origin of pore | Characterization methods | Relative pore radius |
|-------------------|----------------|--------------------------|---------------------|
| Atom and molecule pore | Micropore (<2 nm) | Space among atoms or ions, Crystal lattice, Trace of solvent molecules after drying | <6 |
| Aggregate Molecules pore | Mesopore I (2-10 nm) | Micelle or liquid crystal templating | Gas adsorption, TEM, XRD |
| Liquid phase pore | Mesopore II (2-50 nm) | Phase separation, Space among particles | Gas adsorption, SEM, TEM |
| Spatial pore | Macropore (>50 nm) | Bubble, Cavity, Space among particles, Particle templating | Porosimetry SEM |

Pore radius divided by diameter of nitrogen molecule (0.354 nm)
Synthesizing Atom and Molecule Pore

Zeolite is a typical material in this pore range. It was in 1756 that the Swedish minerologist A. F. Cronstedt was the first to observe that steam was emitted when a mineral called stilbite was heated. On account of this he coined the term “zeolite,” which is a combination of the Greek “zeo” for boil and “lithos” for stone. Since then about 40 kinds of such minerals have been discovered. Today zeolite is understood to be a hydrous crystallized aluminosilicate mineral. Many of these materials are tectoaluminosilicates which, as illustrated in Fig. 3, are $\text{MO}_4$ tetrahedra (M means the Si, Al, or other atom of a tetrahedron) that share their apex oxygen atoms with a neighboring tetrahedron. This means the atomic ratio $\text{O}/\text{M}$ in the frame is 2.

Zeolite is characterized by its uniform pores, which are about the same size as its molecules. Because zeolite can be classified by the size of its molecules, it is also called a molecular sieve. [9] Many types of zeolite have been synthesized, as seen in the industrialization of ZSM-5 (MFI) as a catalyst. In addition to aluminosilicate, zeolite with many different compositions and structures have been synthesized. VPS-5, with pore sizes between 1.2 and 1.3 nm, is the first aluminophosphate zeolite with pore sizes over 1 nm. Its pore walls have an 18-ring structure comprising 18 $\text{MO}_4$ (M: Al, P) units. Gallium phosphate zeolite, which has a 20-ring structure have been synthesized recently. A characteristic is that although the pore entrance size is about the same as that of VPI-5, crystal interiors have voids called supercages as large as 3 nm.

Generally zeolite is made by hydrothermal synthesis. Si and Al sources and crystallizing agents are put into an autoclave, where the materials are dissolved and recrystallized. Any number of different zeolite types may result depending on the ingredient ratios, crystallization temperature, and crystallization time. Table 3 gives the conditions for synthesizing zeolite membranes, which are of particular interest. [10-16].

At the center of attention in recent years is zeolite that can change its pore size in accordance with external fields. Reported types of variable-pore-size zeolite that can adjust its pore size by temperature are aluminosilicate of RHO type, and a type of titanosilicate zeolite. In particular, the titanosilicate whose ETS-4 (Engelhard titanosilicate-4) counter cations have been replaced by strontium is stable under heat treatment and can reversibly and precisely adjust its pore size between 0.427 and 0.394 nm. [17] Further, recent environmental problems underlie frequent reports including those on the synthesis of zeolite from wastes, and there are expectations for increasing research advances in the field of zeolite synthesis.

In contrast with the three-dimensional spaces of zeolite, various attempts are underway to find ways to use the unique two-dimensional spaces of stratified substances, of which the clay minerals are representative. The water-caused swelling of montmorillonite, which has long been known, is a phenomenon that is closely connected to the plasticity of clay. While the distance between layers in dry montmorillonite is
about 0.95 nm, it changes by steps from 0.95, 1.24, 1.54, and 1.90 nm as relative humidity rises. [18] These distances correspond to a compound in which water molecule layers each about 0.3 nm thick make their way between montmorillonite layers in numbers of 0, 1, 2, and 3 water layers, respectively. The interlayer energy balance depends on: 1) inter-layer ions and silicate layer coulomb energy, 2) hydration energy of inter-layer cations, and 3) energy of water adsorption between layers in relation to humidity. [19] Hence, the behavior of change in inter-layer distance is controlled by the types of inter-layer cations and the nature of the silicate layers. [20] Montmorillonite with Na ions between its layers swells without limit under circumstances with much water, as in aqueous solutions, [18, 21] and there are reports that montmorillonite with Li ions between its layers undergoes similar unlimited swelling. [22] Additionally, various organic compounds become the guests of inter-layer substances. There have long been reports of attempts to obtain inter-layer compounds with guest organic polymers by polymerizing monomers between layers. Bentonite, montmorillonite, or other substances in which the inter-layer ions of layer substances have been replaced by ion exchange with cationic surfactant ions are used to put nonpolar organic molecules between layers. However, as illustrated in Fig. 4, limitless swelling is not observed at times like this because, in response to the size of the hydrophobic portion of surfactant ions, the material does not sorb an amount of guest molecules larger than that which is held in the space formed between layers. [19] In recent years there has been much research on the synthesis of intercalation compounds that are good at bringing various substances between layers, as happens in this swelling. In particular there is much research of great interest on providing various functions through surface modification between layer-

![Fig. 4](image-url) Swelling model of toluene to montmorillonite intercalated by trimetyldodecylammonium cations. (modified from Fukushima [19]).
ers for the purpose of achieving molecular recognition and reactions that select certain substances. [23, 24] And in view of aim of this paper, our interest is in methods of synthesizing porous materials through inter-layer bridging, which have been researched for the purpose of molecular sieves. We have already noted that various organic and inorganic molecules are adsorbed between the layers of layered clay minerals, where they push the layers apart, but molecules adsorbed between layers are easily desorbed by washing or heating and exhausting. This makes it hard to use inter-layer adsorption compounds as stable molecular sieves. In that regard, ion-exchanging inter-layer compounds whose intercalated cations maintain a balance with the negative charge of layers will exist stably between the layers unless inter-layer ions undergo exchange or separation reactions with other ions. Shabtai et al. [25] and Mortland et al. [26] reported on inter-layer compounds that made possible a molecular sieve effect by making pillars of ethylenediammonium ions between montmorillonite layers (Fig. 5). This inter-layer compound, whose distance between layers is 0.53 nm, will not break down even if heated to 350°C in air. But in consideration of the usual catalytic reaction or catalyst preparation conditions, organic cation pillars are actually not stable enough as catalysts or carriers. For that reason creative efforts are being made to build sturdy pillars of metal oxides between layers by intercalating inorganic cations. Representative methods include inter-layer bridging by polynuclear inorganic ions, and by sol particles. Using the former method, dropping an alkali into an aqueous solution of a metallic salt will often result in the precipitation of a metal hydroxide. Under conditions in which hydrolysis is insufficient, and just before a precipitate is formed, a number of metal ions gather by using OH group and are present in water as a polynuclear hydroxide ion. [27] $\text{Al}^{3+}$ forms a variety of hydroxide ions, sometimes even bulky ions like $\text{Al}_{13}^{3+}(\text{OH})_{27}^{6-}$. And when $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is dissolved in water, hydroxide ions of $\text{Zr}_4^{4+}(\text{OH})_8^{8-}$ form. A method has been proposed to obtain bridges using metal oxide pillars by intercalating these large metal hydroxide ions between the layers of clay minerals using ion exchange, then firing the compounds between clay layers at high temperature. Brindley et al. [28] and Lahav et al. [29] used this method to prepare a montmorillonite bridge using alumina as pillars. The distance between layers is about 0.75 nm. The specific surface area of this pillared material is about 400 m$^2$/g, which is far larger than the 20 to 30 m$^2$/g of montmorillonite before pillaring. It is also reported that inter-layer distance is almost perfectly maintained even at 500°C, showing that thermal stability is also good. Yamanaka et al. [30] created zirconia pillars between montmorillonite layers and obtained an inter-layer compound with an inter-layer distance of 0.84 nm and a specific surface area of about 500 m$^2$/g. Also reported is a bridge formation method that selectively deposits metal hydroxides only between clay mineral layers, without using ion exchange. Yamanaka et al. [30] prepared nickel oxide pillars between layers and inter-layer distances of 0.52 nm by causing the deposition of nickel hydroxides between montmorillonite layers. Several methods have been devised to intercalate unstable metallic cations in water. For example, ions are introduced between layers in the form of complexes, or first organic materials are inserted between layers, and then the desired ions are introduced. [32]

**Fig. 5** Schematic model of montmorillonite pillared by ethylenediammonium ions (modified from Mortland [37]).

**Synthesis of Aggregate Molecules Pore**

From physico-chemical point of view, gas adsorption has a boundary region in which the micropore filling phenomenon and the capillary condensation phenomenon occur. Attention has focused on the unique structure and synthesis method, making this one of the hottest research fields at present. The inter-layer compounds discussed above become pores in this boundary region, depending on the pillar synthesis method. Here we shall discuss a group of synthesis methods for what are known as mesoporous molecular sieves.

Pioneering mesoporous molecular sieves are FSM - 16 [33-35] and MCM - 41 (M 41S) [36, 37], which were synthesized by an American group and a Japanese...
group, respectively. It is very interesting that these new substances were independently synthesized at about the same time, and it would seem this is closely related to these factors: technical levels had matured to the point making synthesis possible, and there was a strong need for the synthesis of large-pore zeolite.

**Fig. 6** is a block diagram illustrating the synthesis processes and conditions of these large-pore zeolite. Basically they are synthesized in a series of operations in which layered silicate, tetraethyl orthosilicate, silica, or other Si feedstocks are heated for several hours to several days at 70 to 150°C in a surfactant aqueous solution, after which the solid products are filtered out and fired at 550°C or higher. When making FSM-16 the process of synthesizing layered silicate comes in the first half. At first glance this appears to be a useless process, but its advantage is that one can obtain a highly crystalline product with processing at lower temperature and shorter time than MCM-41. **Fig. 7** schematically models the synthesis mechanism of FSM-16. Kanemite is a clay mineral consisting of single-layer silicate sheets having Na ions between layers. Ion exchange introduces alkyltrimethylammonium (ATMA) between kanemite layers, whereupon the silicate sheets bend and form composites with ATMA. Next, dehydration and condensation of silanol radicals bridge the layers, resulting in a three-dimensional framework. This is a new inorganic synthesis method that demolishes the traditional concept of crystal synthesis methods by crystal growth. By contrast, the MCM-41 synthesis method is a process which, like the traditional method of synthesizing zeolite, basically puts the raw materials into a sealed reactor and heats them at a temperature and for a time that are appropriate. This method is illustrated in **Fig. 8**. [37] Varying the
ratios of ATMA, Si, and NaOH in the ingredients makes it possible to control the structure into hexagonal, cubic, sheet, and mesostructures. [40, 41] Micelles form when the surfactant exceeds the critical micelle concentration (CMC) in an aqueous solution. It is known that further raising the concentration over the CMC forms self-organizing molecular aggregates (liquid crystals) such as hexagonal, cubic, and sheet forms. [42] This is probably the reason that the mesopore family M 41S synthesis mechanism, of which MCM-41 is representative, is known as the "liquid crystal templating (LCT)" mechanism, because the liquid crystal structure of surfactant become as a mold. [37] Like FSM-16, when synthesizing M CM-41 the pore size is controlled by changing the length of the ATMA alkyl chains. [37] And instead of using ATMA, the addition of mesitylene will further enlarge pore size to a maximum diameter of 10 nm. [37]

Little time has passed since these substances were first synthesized, but despite the many reports of applied research, they have yet to see practical use. We hope to see the industrial implementation of these unique structures.

Synthesis of Liquid Phase Pore

Pores discussed in this section are those of the size range in which capillary condensation occurs, and the molecules trapped inside the pores generally behave as liquid. Typical of the porous material manufacturing methods in this area are those which use the unique phenomenon called glass spinodal decomposition, developed by Dow Corning Corp. The typical synthesis process is as follows. [43] SiO2, H2BO3, and NaCO3 are used as the main ingredients to make Na2O-B2O3-SiO2-based borosilicate glass, which is made into forms such as tubes and plates. In these forms it is the borosilicate glass shown in Fig. 9a. To separate the phases, the product is then heat-treated at several hundred degrees, which yields a B2O3-Na2O-rich glass phase and a SiO2-rich glass phase whose sizes are on the order of several nm (Fig. 9b). The B2O3-Na2O phase is dissolved in an acid solution or hot water, where dissolution is performed to yield porous glass with a high SiO2 content (Fig. 9c). The result is a porous material whose molded shape is retained and which has countless perforations.

There is also a method of making porous silica materials by inducing phase separation with a chemical trigger. Nakanishi et al. [43] report on a method that uses water-soluble polymers to induce phase separation in a sol-gel silica system. Water-soluble polymers can be classified into two groups. First, as is typical of polyacrylic acid, polymers having comparatively weak attractive interaction with silica are mainly partitioned into a different phase from silica when phase separation occurs, and the polymer-rich phase forms pores. Second, surfactants, and polymers that include polyoxyethylene units are partitioned into the same phase as silica owing to the formation of hydrogen bonds with silanol radicals. Therefore it is mainly the phase comprising the solvent phase that becomes pores. There are also reports that various pore sizes and structures can be obtained by adjusting hydrolysis conditions and solvent polarity. [45] Fig. 10 shows the steps in the synthesis method. Silica alkoxide (tetramethoxysilane, TMOS or tetraethoxysilane (TEOS)) is blended into a mixture of an acid catalyst and a solution in which an organic polymer is uniformly dissolved, and a hydrolysis reaction yields a product which is then gelated and matured under sealed conditions. After performing solvent

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**Fig. 9** Production process for porous glass (modified from Makishima [43]).
exchange if necessary, it is dried to obtain a porous material. The porous silica produced by this method finds increasing use as monolithic HPLC columns and in biology-related fields.

**Synthesis of Spatial Pore**

This is a group of porous materials with so called macropores, a range of pore sizes in which the capillary condensation phenomenon is no longer observed physico-chemically. For that reason pore characteristics are assessed mainly with the mercury porosimetry. Additionally, such materials have been made for a long time, and applied in many ways. There are many industrially important materials. Diatomaceous earth, which is the skeletons of diatoms, is well known as a natural mineral of this group having uniform pores of about 1 µm. The diatomaceous earth, after having been fired organic contents, is applied to filtering auxiliary for brewer’s yeast, and moisture-adjusting building materials. [47] Various methods of making artificial macroporous materials include primitive methods that simply use the interstices between particles, methods that maintain the pores in a formed material by low-temperature sintering, and methods that impregnate organic objects having reticulate structures with ceramic slurry, then firing to eliminate the organic material and leave pores (replica method). [48] Another method entails embedding a ceramic or polymer matrix in the interstices of a packed particle structure, then removing the particles by either firing or using a solvent to dissolve them out. [49-51] With this method, pore size and structure are determined by the particle size and coordination number. When a structure is uniformly packed with particles of a uniform size, uniform macropores will be formed. This method is spotlighted also as a method of making gas sensors and bioceramics. [52] A similar method is proposed that uses fibers in place of particles. Here we shall discuss methods using new and old forming agents, and the synthesis of porous materials using an in situ solidifying method, which is promising as a new porous material manufacturing process.

Autoclaved lightweight concrete (ALC) is one porous material made with blowing agents. ALC is a material derived from the sand-lime bricks that were long manufactured in Europe. It is made from about the same raw materials as the bricks, and is impregnated with bubbles for lightness. ALC was first made in 1929 by the Swede Ytong, and similar techniques then spread to other regions, primarily in Europe. In 1963 it came to Japan and its use widened. Common to these manufacturing methods is autoclave processing that uses siliceous and calciferous materials, but raw materials vary from one company to another.

We shall describe A manufacturing process. [53] The raw materials silica (50 to 70%), quicklime (5 to 20%), portland cement (10 to 40%), gypsum dihydrate (2 to 10%), and metallic aluminum (under 0.1%) are made into a slurry, which is put into molds after kneading well. The quicklime slurry is digested and becomes slaked lime, and the cement begins hydration. As this time, the metallic aluminum serving as the blowing agent evolves hydrogen gas, resulting in green body that are lightweight owing to the bubbles produced by forming. After demolding, the green body are cut to the prescribed thickness and treated for 5 to 10 h in an autoclave at about 180°C and under saturation vapor pressure, yielding finished ALC products. In terms of chemical reactions, at the green body formation stage the ALC manufacturing process involves mainly the hydration of cement that forms high-calcium-content calcium silicate hydrates and Ca(OH)₂. High-calcium-content calcium silicate hydrates are also formed at the autoclaving stage. It is thought that hydrothermal reactions finish when the CaO supply is completely consumed, which means that some of the silicate in the SiO₂ supply is left unreacted. Usually the silica reaction rate is thought to be 40 to 60% A major drawback of ALC is its water absorptivity. Its water retention has adverse effects such as freezing damage. Recently innovative steps are taken, such as making the product water-repellent.

Of particular interest in recent years as a forming metal manufacturing method is the slurry forming
In this method, a surfactant and an evaporating forming agent (a hydrophobic volatile organic solvent) are added to a water-based slurry containing metal powder. After formation, the forming agent is volatilized and its vapor pressure directly forms bubbles in the slurry. This is dried, degreased, and sintered to yield the final product. The pore size is controlled in the slurry forming process, whose mechanism is pictured in Fig. 11. A slurry is created with a water-based binder, and a surfactant and forming agent are added in amounts sufficient to form bubbles in the entire slurry. The surfactant makes the forming agent dissolve into the slurry, and the particles disperse (Fig. 11a). Raising the temperature causes the forming agent to gradually volatilize and form bubbles (Fig. 11b). The aqueous surfactant solution membrane makes the bubbles into isolated bubble aggregates, and the metal powder agglomerates in the spaces between bubbles. In the subsequent drying process the bubble aggregates arrange themselves in a three-dimensional reticulate configuration, and the solid components form a spongelike structure (Fig. 11c). Exercising strict control over slurry viscosity, surfactant types, forming agent amount, forming time, drying time, and other factors makes it possible to create various pore sizes and pore structures.

There is also a unique method known as solid-gas eutectic solidification that uses gas solubility to make metallic porous materials called gasars. This method takes advantage of the fact that when the solubility of gas atoms in a molten metal is high, but their solubility in the same solid metal is low, the gas atoms that could not completely dissolve when the metal solidified become bubbles. [55] Just as with the hydrogen gas solubility in Mg, Ni, Fe, Cu, Al, Co, W, Mn, Cr, Be, and Ti, or alloys of these, metals which have large gas solubility differences between their solid and liquid phases readily form bubbles and yield porous products. It is also possible to control the orientation in which pores are formed by making a certain part of the mold cool, which cools the molten metal in a certain direction after it is put into the mold. Fig. 12 schematically illustrates a mold constructed so that the bottom is partially cooled, and the product obtained with that mold. Making porous products with this method allows one to freely control pore orientation, pore size, and porosity by controlling a variety of parameters including melting temperature, cooling rate, pressure of ambient gas while being dissolved into metal, mixing volumetric ratio and pressure of inert gas, and gas pressure when solidifying. [56]

We shall now discuss methods of synthesizing porous materials by using in-situ solidification, developed as a gel casting method by Oak Ridge National Laboratory in the US. [57, 58] This method entails preparing a ceramic slurry into which monomers...
have been dissolved, putting the slurry into non-porous molds, and then polymerizing the monomers, resulting in the formation of a polymer network in the dispersed medium, and yielding a molded wet product. This method offers the following advantages. [59] (1) Because slurry production is basically the same as casting, the method can be used if a high-concentration slurry is made; (2) molds of complex forms can be used, and near-net shaping is possible; (3) because the fluid and solidification processes can be kept separate, and because the ceramic particles are fixed in situ, unevenness and flaws occur in molded products only with difficulty; and (4) the small amount of organic binder in the molded product makes degreasing easy.

The in situ solidifying method makes it possible to obtain porous products because its series of processes introduces bubbles into the pre-polymerization slurry and then begins polymerization. [60] We explored the use of this method in creating porous ceramic materials which have high porosity and whose pore structure is controllable, and we succeeded in raising porosity to 80% or more even though it was limited to 50% with traditional methods.

We further reported that it is possible to control porosity, pore size, and other properties by taking into consideration the type of frother and the polymerization time. [61] In terms of strength as well, this method is superior to low-temperature firing and the replica method because in low-temperature firing the matrix does not completely assume a minute structure, and because with the replica method small cracks form in the matrix when the large amount of organic material decomposes. Innocentini et al. [62] report that porous materials made by gel casting have higher strength than those made by the replica method.

**Fig. 13** shows the basic process of a porous material synthesis method that employs in situ solidification. First, a slurry of ceramic powder, distilled water, monomers, and other ingredients is prepared. A surfactant is added as a frother, and foaming is induced by mechanical stirring. A polymerization initiator and a catalyst are then added to the bubble-impregnated slurry, after which it is poured into molds. After hardening, the molded wet product is demolded, dried, degreased, and fired to yield a sintered porous product.

![Fabrication route of porous solid material by applying in situ solidifying method (modified from Sepulveda [60]).](image-url)
Fig. 14 shows a porous item made with this method. Research and development are underway for applications of these porous materials as high-temperature filters and various ultra-light building materials. It is also thought possible to create processes which take into consideration resource-cycling systems that include the productive use of wastes as raw materials, and reduced energy use. We hope that in the near future readers will find in their midst porous materials made with this method.

Conclusion

Porous materials can be conceived as composites whose first component is their solid portions, and whose second component is the air phase in their pores. Hence it is perhaps beneficial to incorporate composite characteristics and function expression mechanisms as guidelines for designing porous materials. While dispersed composites assume various structures depending on the properties, state, and form of their materials, two-phase composites are classified by the structural models in Fig. 15. [63] As this shows, the spatial connection state of each component, which can assume the zero, first, second, or third dimension, determines the type (m-n) of composite by the connection order of each component. Usually m is assigned to the functional component and n to the inactive component. For example, in a (0-3) type composite the functional component is isolated and dispersed, and the matrix component is connected in three dimensions. In other words, this porous material can be seen as having closed pores. Here we have shown only the structures, but readers can see that many other findings on composite materials can be turned to use as shared concepts for the development and manufacture of porous materials.

The functions of porous materials are affected not only by pore size, but also by pore structure and other attributes. Incorporating methods of analyzing composites' physical properties should bring about progress in the assessment and analysis of porous materials. While our insufficient efforts are partly to blame for not being able to include these here, another reason is that often a number of factors underlie the function expression mechanisms of porous materials, and they have yet to be sufficiently analyzed. From another perspective this suggests the possibility of discovering many as yet unknown porous material properties.

This has been a review of porous materials that interest the authors. We hope this explanation will help people who are working on the design of new porous materials.

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