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Porous Sol–Gel Ceramics

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Abstract: Ceramic gels are composed of colloidal particles or polymeric macromolecules aggregated in a three-dimensional very open network. This paper addresses the network architecture of porous materials which can be made from these gels. The main parameters which have an influence on the pores, during the low temperature chemical procedure, as well as during drying or heating, are reviewed. The variety of feasible structures is illustrated on a few examples. The applications, such as in catalysis and filtration, are summarized. © 1997 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Porous ceramics are interesting materials for advanced applications which require a diversity of products such as ionic conductors, filtering membranes, catalysts, coatings with special optical properties and insulating aerogels. To control the morphology of these porous structures it is possible to adapt a low temperature synthesis process such as sol–gel, to submit the material to an appropriate heat treatment and to make more complex agencies with gels and fine particles.

2 STRUCTURE OF CERAMIC GELS

Gels are monolithic materials with an elastic network which may be organic or inorganic. In both cases, this solid network may account for a very small volume proportion of the monolith, such as a few percent.

A classification of the gels in four classes was proposed by Flory.[1] It is comprised of (Fig. 1): (1) lamellar gels, such as pitch mesophase; (2) covalent polymeric gels largely represented in organic chemistry; (3) physical polymeric gels made by crystallization of polymeric chains in local areas; (4) particulate, or colloidal gels, in which dense colloidal particles of various shapes are linked to each other so as to form a very porous three-dimensional (3-D) network.

In ceramics, most gels belong to the 4th class in Flory's classification. However, ceramists distinguish two classes of gels which they term polymeric gels and colloidal gels, respectively. Colloidal gels comprise two phases in the thermodynamic sense: the solid phase in the 3-D network and the liquid phase of the matrix. On the other hand, true polymeric gels according to the definition by Flory only contain one phase as in a solution, except that the solute molecule is replaced by an infinite 3-D elastic network. This network has a linear polymeric nature, with some branching points, instead of being composed of solid particles with a 3-D size. Actually, ceramic gels which are termed polymeric by ceramists do not have a well defined linear atomic chain structure, such as in the organic polymer gels. However, their classification as polymeric gels by ceramists is justified because it is not possible to observe two phases in the thermodynamic sense, by any microscopic technique. In the following text, the term polymeric gels refers to the classification by ceramists.

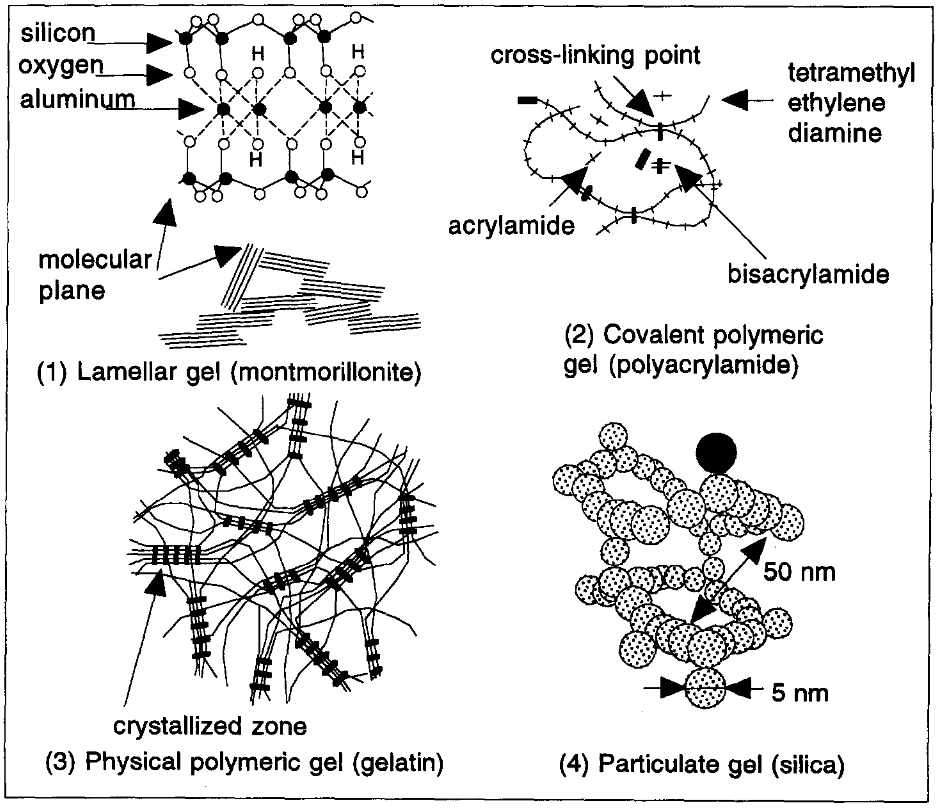
After carbon, the cation most prone to build linear covalent polymers is silicon. Polymeric silica gels can be made from silicon alkoxides with the help of acid catalysts. Mixed component gels, where SiO_2 is the major component, also form polymeric gels. Boron is another cation which easily forms polymeric gels.[7] Polymeric gels which are water soluble (as in Flory's 3rd type) can also be made from aluminium alkoxides near 20 °C in the presence of nitric acid.[8]

The X-ray diffraction pattern of a polymeric gel is amorphous and it differs from that of a glass by the presence of a central diffusion peak due to pores smaller than 10 nm. However, an amorphous X-ray diffraction pattern does not necessarily indicate that a ceramic gel is polymeric, since colloidal particles or fibres can also have an amorphous structure.

Colloidal ceramic gels have a coarser structure than polymeric ceramic gels. The particles in the solid network and the pores are bigger in colloidal gels than in polymeric gels. The network structure is to a large extent influenced by the fabrication method and by polymeric or electrolyte additives, which adsorb on the surface of the particles. These two types of additives introduce interactions between the particles, which are termed steric and electrostatic, respectively. Such interactions are addressed in detail in many publications and books and they are not the subject of the present paper. However, their influence on the pore structure in a gel is important and it is illustrated in Fig. 2 for spherical colloidal particles in the case of electrostatic interactions.

In this figure, the pH is such that spherical particles are positively charged, so that they are surrounded by a negative electrical counter-ion layer. A concentration, C, of indifferent electrolyte can be added to the colloidal suspension. When C is lower than the critical coagulation concentration, C_c, the repulsion barrier to a contact between particles is thin. Particles can pack randomly and the average distance between nodes (branching points) in the packing networks is small. When $C_g < C < C_c$, where C_g is the critical gelation concentration, a colloidal gel is formed. For $C < C_g$, no gel is formed, the particles remain dispersed. The network formed by the colloidal particles is more and more open as C gets closer to C_g, so that the average distance between nodes (branching points) increases. The specific surface area is usually higher in a gel than in random packing. However, the specific pore volume is also higher. Actually, the average pore size is larger in a colloidal gel than in random aggregates, and this difference is maintained even after heat treatments at fairly high temperatures.

For plate-like particles, the variety of possible particle association modes is even larger, as illustrated in Fig. 3. Regarding the pore shape, the association mode (a) in Fig. 3 can provide fine planar pores, and a solid network structure with a highly preferred orientation. The association mode (b) can lead to a type of packing known as "card-house", where the pores have a roughly isometric shape. The association modes (c) and (d), such as edge-to-edge, can lead to a more or less random and open random aggregation. They also make it possible to build rather linear strings of particles, as in the colloidal silica gels.



(1) Lamellar gel (montmorillonite)

(2) Covalent polymeric gel (polyacrylamide)

(3) Physical polymeric gel (gelatin)

(4) Particulate gel (silica)

Fig. 1. The gels in the classification by Flory, after Pierre:[2] (1) montmorillonite lamellar gel, after Pierre and Uhlmann;[3] (2) covalent polyacrylamide gels, after Tanaka;[4] (3) gelatin gel, after Gerngross and Herrmann;[5] (4) particulate silica gel after Fricke.[6]

In most cases, the pore microstructure of a ceramic gel is too fine to be observed under an electron microscope. This is typically the case with colloidal silica gels dried in hypercritical conditions, which is illustrated in Fig. 1(d). The mass, M, of the gel solid network inside a sphere of radius R, from any centre in the gel network, and for a radius up to 200 nm, increases in average as:

$$M \approx R^f \tag{1}$$

In this equation, f does not have the usual value of 3. Instead, f is not an integer, and it is termed the "fractal dimension".

A silica aerogel, as any aerogel, is a dry gel which can be described as a fractal construction, but only in a limited scale range. The pores are very small inside primary spherical aggregates which have a radius of the order of 5 nm in the silica gel in Fig. 1. Outside these primary aggregates, the pore dimension drastically increases. Fractal structures could be observed directly in gels made by aggregation of colloidal gold particles with the help of an organic ligand.[10] Similar structures were observed in colloidal montmorillonite gels, as illustrated in Fig. 4.

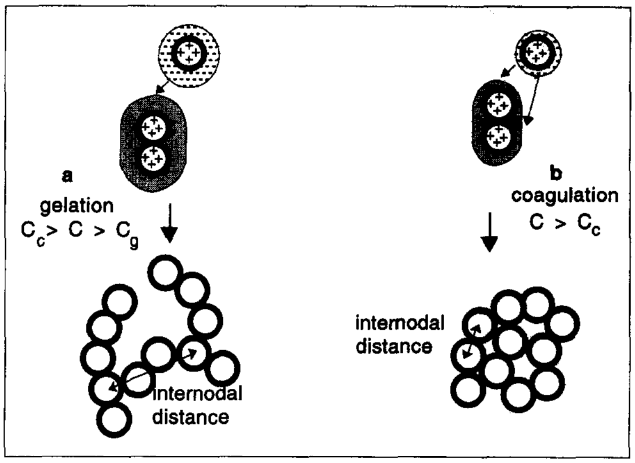


Fig. 2. Evolution in the pore shape built by spherical colloidal particles as the repulsion barrier to contact increases in thickness, in the case of electrostatic interactions. C is the concentration of a non-potential determining electrolyte.

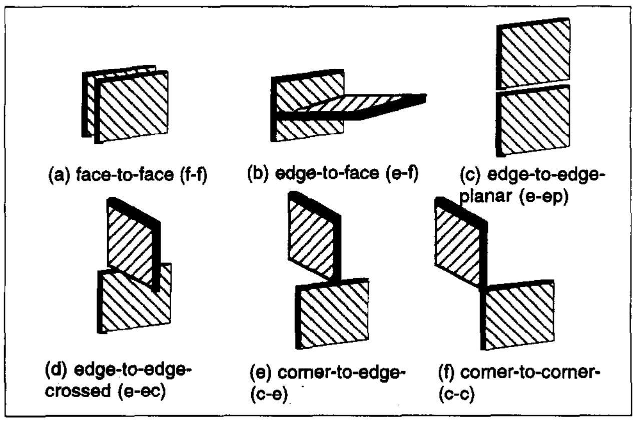


Fig. 3. Possible association modes of plate-like particles with electric charges of the same sign on both edges and faces (after Pierre[9]).

Generally speaking, the pore structure drastically depends on all the parameters in the sol–gel chemistry, such as the pH, proportion of water used for hydrolysis, presence of an acid or base catalyst, dilution of the reactants and nature of the solvent.[12] For instance, the density and refractive index of silica aerogels increase, and their specific surface area and pore volume decrease, as organic solvents with an increasing chain length and increasing branching are used.[13] Besides, acid catalysed silica aerogels have smaller pores than base catalysed aerogels. However, base catalysed gels are more branched on a short scale and they have a higher specific surface area.

Colloidal gels obtained from the aluminium alkoxides are formed in acidic conditions. They are composed of colloidal boehmite particles with a plate-like shape. However, their structure is too fine to be observed under a scanning electron microscope. In containers where the particles stick to the bottom, such as in glass dishes, a marked preferred horizontal stacking of the boehmite layers occurs during drying and thin gel films are obtained. Such a film is shown in Fig. 5(a). The film X-ray diffraction data shows a very intense (002) interlayer peak,[3] in comparison to the X-ray data on a powder from the same sample [Fig. 5(b)]. Such a film can also swell in an aqueous medium, which makes it possible to observe parallel stacking of packets of layers on the edge of the boehmite film, using SEM [Fig. 5(c)]. Packets of layers can be peeled off from the film by bending it, as illustrated in Fig. 5(d).

It is interesting to note that because these flat lamellar boehmite gels, as well as some aluminosilicate gels of the montmorillonite variety, have a layered microstructure which swells in water, they

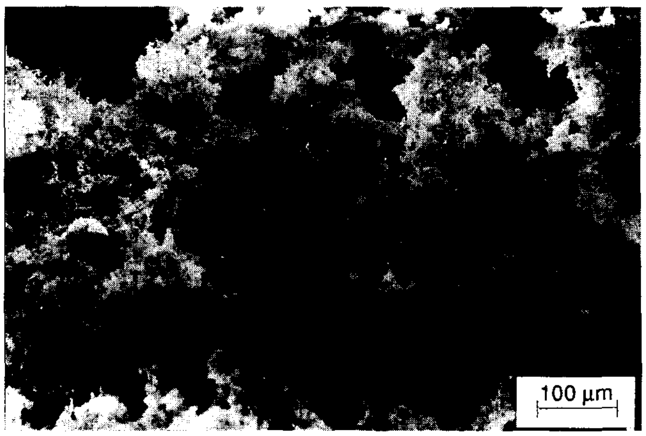


Fig. 4. Fractal agglomeration in a montmorillonite gel (after Pierre *et al.*[11]).

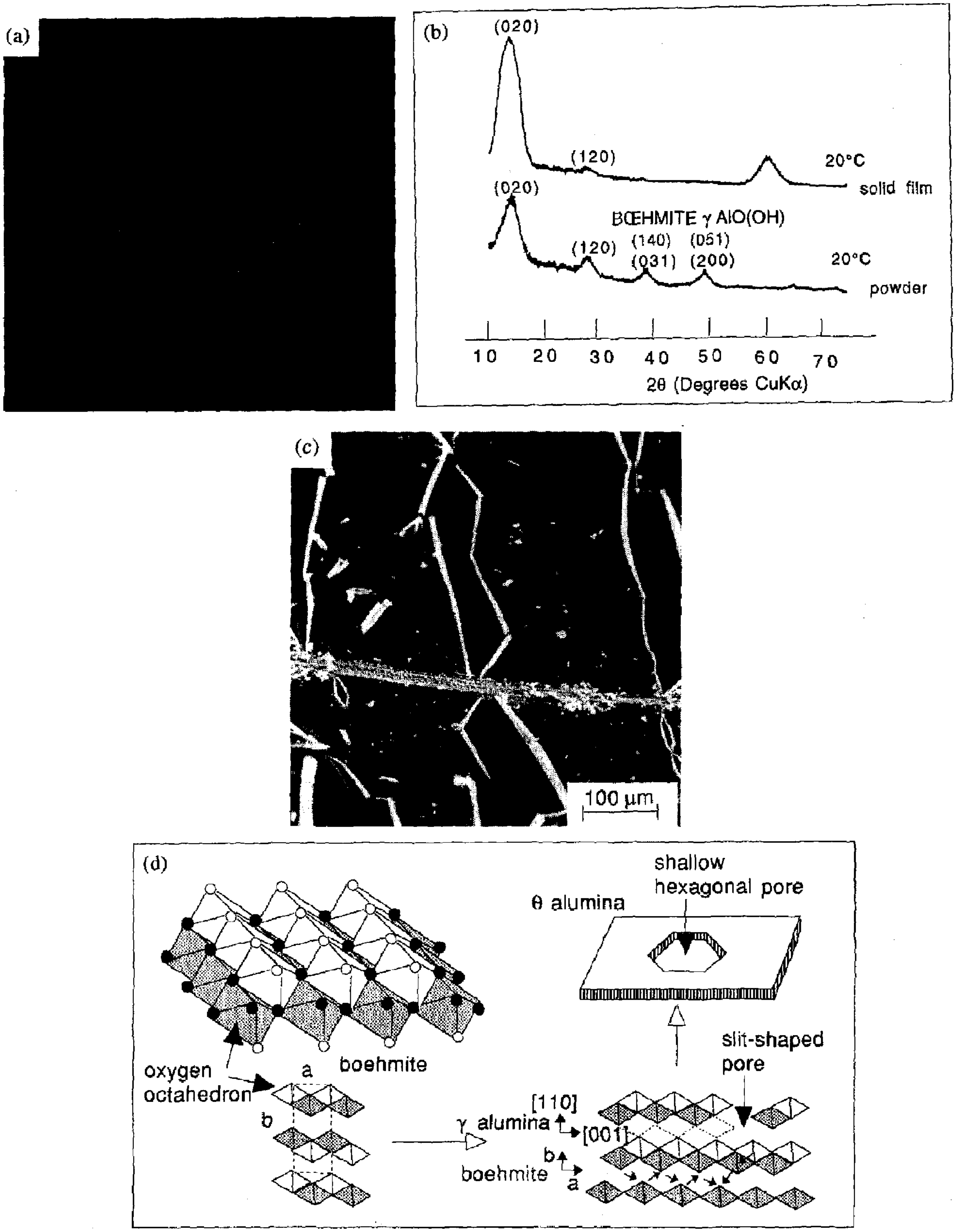


Fig. 5. (a) Boehmite gel film; (b) X-ray diffraction of the film and of the powder from the film; (c) edge of the film in an SEM; (d) peeling of layers from the face of the boehmite film submitted to flexion, in an SEM (after Pierre[2]).

could be classified as belonging to the 1st class in the classification by Flory. However, they also definitely belong to the class of colloidal gels for the ceramists.

The porous structure of ceramic gels, such as SiO_2 or TiO_2, can be modified in many ways which include aging in their mother liquor, drying and heat treatment. In their mother liquor, these gels undertake a slow evolution termed syneresis. During this evolution, a gel monolith does not change shape, but it slowly shrinks. The smallest pores are partly eliminated and partly closed, while the smallest particles in the network fuse together.

Drying by evaporation can also modify to a large extent the pore network of a gel, because liquid–vapour menisci are created at the exits of the pores. These menisci induce a hydrostatic tension in the liquid, which is balanced by an axial compression on the solid network of the gel. In turn, the compressive stresses make the gel shrink and the pore size decrease. To maintain a fine pore structure, it is necessary to decrease the surface energy of the liquid matrix as much as possible. This can be done with chemical additives such as the surfactants. However, the effect of surface tension on the pore size is complex. For instance, in silica gels, Smith *et al.*[14] found that the specific surface area (S_a) of base catalysed, as well as acid catalysed, gels decreased as the surface tension of the mother liquor increased. However, in these acidic gels, the micropore specific area (pores smaller than 2 nm according to the IUPAC definition of micropores) and volume increased as γ increased. As the acid catalysed gels are less cross-linked than the base catalysed gels, this difference may be related to a different rigidity of the solid network.

The ultimate aim of obtaining a high pore volume, together with a high specific surface area, is achieved by performing hypercritical drying (or supercritical drying), in which the surface tension of the liquid is cancelled ($\gamma = 0$). This technique was first investigated by Kistler[15] in 1932. It requires one to heat the gel at a temperature and pressure which exceed the critical point of the liquid matrix. The hypercritical fluid is then evacuated as a gas by flushing with dry argon. Large dry gel monoliths with a specific area over 800 m^2/g were reported.[6] The supercritical drying conditions are important. In TiO_2 aerogels dried in CO_2, the pore volume increased and the pore size distribution broadened, while the specific surface area was not significantly affected, as the supercritical drying temperature increased from 343 to 473 K.[16] With this technique, the sol–gel chemistry is also important. As an example, concerning alumina aerogels made from Al–*sec*-butoxide in 2-propanol, Astier and Sing[17] reported that the BET specific surface area was high (800 m^2/g) when hydrolysis was carried out with a stoichiometric proportion of water, and lower with a water proportion six times the stoichiometric proportion. On the other hand, after heat treatment at 740 °C, the gel made with the higher water proportion had the highest specific surface area, and its pore size was uniform.

3 TRANSFORMATION OF GEL NETWORKS DURING HEAT TREATMENT

A gel heat treated at increasing temperatures transforms to a more stable solid phase. This evolution involves a chemical modification, a crystallographic transformation of the solid matter and a reorganization of the solid network and of the pore geometry.

At temperatures below 1000 °C, the phases which often form are not the most stable thermodynamic phases. Instead, the formation of a metastable phase can occur, and it may possibly be a crystalline transition phase or a glassy phase. In this temperature range, the transformation is particularly well known for boehmite AlO(OH).[18] In the first stage, the transition γ-alumina is formed according to the reaction:

$$2[\gamma AlO(OH)] \Rightarrow \gamma Al_2O_3 + H_2O \qquad (2)$$

The OH groups on the surface of each atomic boehmite layer combine to produce water molecules which are expelled. The oxygen anions which are not involved in this dehydration basically remain unaffected. Hence, the type of anion crystallographic packing and the crystal boundaries fundamentally remain unchanged. Such transformations are known as topotactic transformations. δ-Al_2O_3 and θ-Al_2O_3 form near 600 and 900 °C, respectively, and they only derive from γ-Al_2O_3 by order–disorder reorganization of the cations.

Concerning the pores, a practical consequence of the loss of structural water is that the material shrinks. Also, electron microscope investigations on boehmite monocrystals showed that slit-shaped pores in the nm size range develop inside each monocrystal. These slit-shape pores progressively merge into bigger and more shallow hexagonal units inside the corresponding δ-Al_2O_3 and θ-Al_2O_3 monocrystals. This pore formation process partly balances the boehmite layer collapse internal to each monocrystal, so that the specific surface area remains high, of the order of 150 m^2/g.

The structure of a gel-derived ceramic depends on the nature of the cations in the solid network. For instance, typical evolutions for the pore size of

TiO_2, ZrO_2 and Al_2O_3 sol–gel material, are shown in Fig. 6, after data from Ref.[20] The pore size remains narrow up to a heat treatment temperature which depends on the material. Usually, the sintering temperature of sol–gel ceramic filtration membrane must not exceed 400 °C with TiO_2, 600 °C with ZrO_2, and 900 °C with Al_2O_3. In CeO_2, all open pores disappear near 300 °C. Hence, the sequence of topotactic transformation which occurs during heat treatment depends on the gel. Silica gels only crystallize at a relatively high temperature, of the order of 700 °C. A marked central diffusion peak is observable below this temperature, which indicates that the material pores are micropores.

Nucleation and growth of a stable crystalline phase occurs at a higher temperature than the temperature where topotactic transformations operate. For instance, the stable α-Al_2O_3 phase forms above 1000 °C by nucleation and growth from the θ-Al_2O_3 transition structure. When nucleation becomes possible, the α-Al_2O_3 grains quickly grow at the expense of a population of former θ-Al_2O_3 crystallites, so that a pore network is entrapped inside each α-Al_2O_3 grain [Fig. 7(a)]. The selected area electron diffraction pattern of the area in Fig. 7(a) shows the spot pattern of a monocrystal [Fig. 7(b)]. Hence, Fig. 7(a) shows a single big grain with pores inside the grain. The pore size is bigger than in the transition phases, while the specific area is much lower.

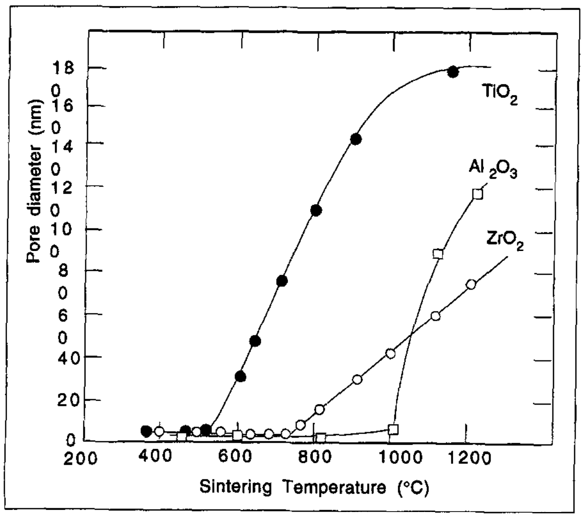


Fig. 6. Pore diameter as a function of sintering temperatures for sol–gel ceramic membranes.

This is consistent with an analysis by Brook.[21] A sufficient number of pores must be present at grain boundaries, and the mobility of these pores must be sufficiently high so as to remain at the grain boundaries during grain growth. In the case of transition alumina derived from boehmite gels, the pores are as large as the grains. Hence, these pores are unable to stop the grain boundary migration, when α-Al_2O_3 forms above 1100 °C.

In agreement with this analysis, foreign additives can significantly affect the phase transformation, as well as the pore structure, at high temperature. For instance, Al_2O_3 aerogels from Al-*sec*-butoxide doped with yttria, transform to the α-Al_2O_3 at a higher temperature (1250 °C) than pure Al_2O_3 aerogels, and they also maintain a higher specific surface area at 1200 °C (88 m^2/g).[22] $NiAl_2O_4$ spinel from aerogels maintain a specific surface area of 63 m^2/g at 800 °C, in comparison to a few m^2/g-loss for the same compound made by conventional processing.[23] One of the highest specific surface areas obtained at high temperature is with Ba hexa-aluminate. Its value is > 10 m^2/g after firing at

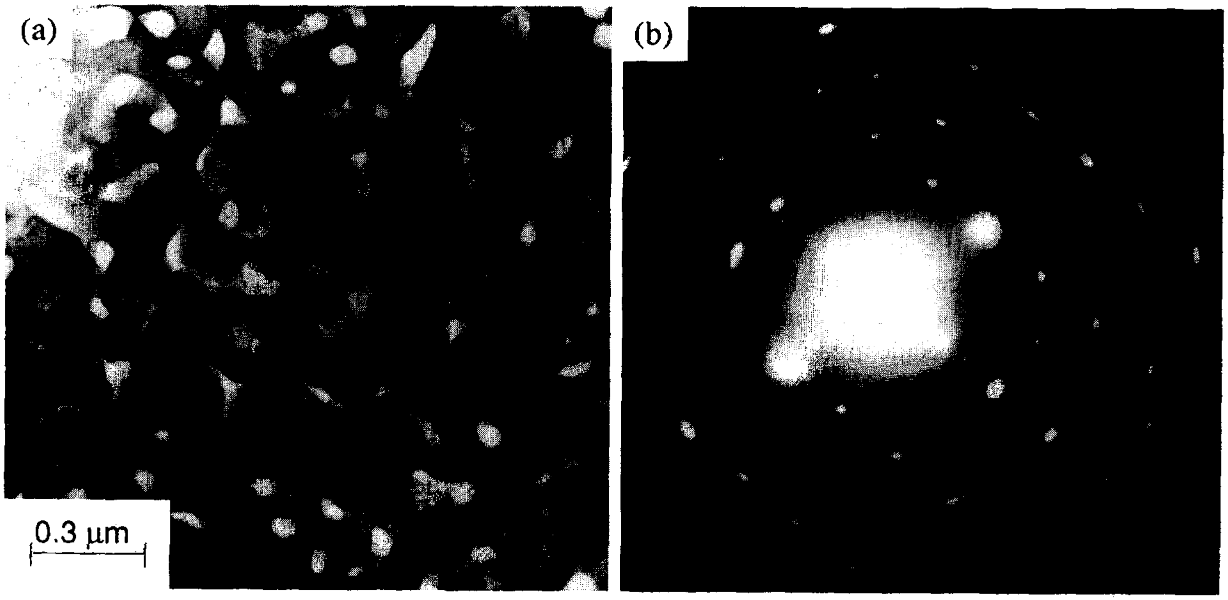


Fig. 7. (a) Porous α-alumina grain from boehmite gel; (b) selected area electron diffraction pattern of the entire grain (after Yang *et al.*[19]).

1600 °C in air.[24] Such materials are very important for the clean combustion of gasoline and diesel engines.

In the case of networks composed of conventional particles (particles bigger than in colloids), the evolution is such that it improves the local symmetry in the alignment of particles. For instance, Petzow and Exner[25] showed, on models with two unsymmetrical particles with respect to their centre, that the particles rotate in such a way as to reach a more even angle on all sides. Three particle models showed that the angle between the lines joining the spheres centres, first begins to increase, then it decreases. Computer simulations on networks with a large number of particles by Ross *et al.*[26] showed that the particles improved their alignment in strings, and they formed "star-like" networks. The direct extrapolation of these results to colloidal particles is questionable. However, colloidal networks undertake a complex evolution during sintering, and it can be argued this evolution can be described to some extent in terms of the local symmetry in the alignment of particles.

4 APPLICATIONS OF CERAMIC GELS

The solid network of a wet gel makes it possible to combine the shaping capability of a solid, and the liquid transport properties of the matrix. This solid network includes dangling ends, termed inactive branches, which are only linked at one end to the main gel network. These inactive branches participate in the density, the pore size and the specific area of a dry gel. They also act as barriers to the diffusion of species (molecules, colloidal particles) within the liquid matrix of the gel. However, they do not modify the properties of a gel, such as its elasticity or its electrical conduction.

Wet SiO_2 gels have found an application as media for the growth of crystalline particles,[27] and in chromatography. In these applications, the gel network is utilized as a barrier to the diffusion of particles, that is to say as a medium to grow all kinds of organic or inorganic monocrystals. The polycrystalline aggregation is made impossible by the gel network, while the diffusion of small molecular species is as fast as in a pure liquid, and it is not disturbed by convection.

The porous structure of sol–gel materials is convenient to intercalate a large variety of compounds for a range of applications. For instance, wet boehmite gels with a highly preferred orientation of the boehmite layer can be made. Since these gels swell in polar solvents such as water, all kinds of electrolytes can be infiltrated between the boehmite layers. Ionic conductors can also be synthesized in this way. For instance, Fig. 8 shows a very porous hybrid polyethylene oxide–TiO_2 material, with nanoscale TiO_2 fibres. Such a material can be reversibly intercalated with Li^+ cations, which makes excellent mixed electronic–ionic conductors.

Dry aerogels also present quite interesting properties. In spite of their high porosity, they are transparent, since their grain and pore size are smaller than the wavelength of visible light. Consequently, they are used as unique optical media in Cerenkov counters in high energy physics,[29] because they make it possible to cover a continuous range of refractive indices from 1.015 to 1.06. They are also used as insulating coatings on windows,

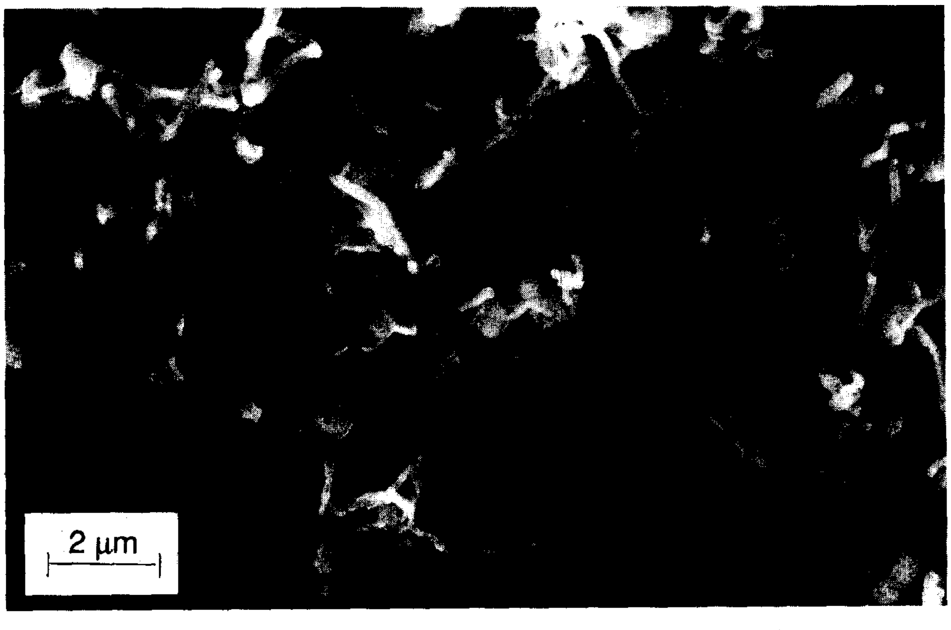


Fig. 8. Hybrid polyethylene oxide–TiO_2 nanocomposite before insertion with Li^+ (after Pierre *et al.*[28]).

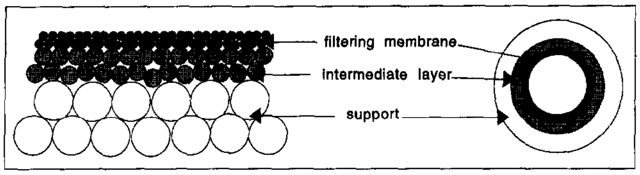


Fig. 9. Cross-section of an asymmetrical ceramic membrane.

because they let the visible light enter a building and they absorb infra-red radiation, that is to say heat, coming from inside the building. Moreover, they are excellent thermal insulators with a thermal conductivity, λ, ranging from 0.01 to 0.02 W/m·K. The low thermal conductivity of aerogels is related to a very low sound velocity v, which is below 100 m/s. Hence, aerogels are outstanding acoustic insulators. They can be applied in acoustic delay lines and in piezoactive antireflective acoustic coatings of thickness λ/4.

In another application, hollow glass spheres with a diameter of 80–100 μm can be made by inflating particles with the gases originating from the gel. These hollow spheres can store deuterium and tritium in nuclear fusion.[30]

Gel derived ceramics are particularly interesting in filtration operations.[20,31] Membranes with pores smaller than 1 nm are used in the technique of reverse osmosis. When the pore size goes from 1 to 100 nm, the filtration technique is known as ultrafiltration. In the size range from 100 nm to 10 μm this is microfiltration, and with larger pores this is simply filtration. These pore size classifications must be compared with the official IUPAC convention, according to which micropores are smaller than 2 nm, mesopores have a size from 2 to 50 nm, and macropres are bigger than 50 nm.

Ceramic membranes can be made by several techniques. However, sol–gel membranes are particularly efficient in ultrafiltration. In most cases, the membrane comprises a thin porous ceramic layer derived from gel, and deposited by a technique such as dip-coating on a ceramic substrate with coarse pores, made for instance by slip casting (Fig. 9). For instance, the combination of a polymeric silica gel and colloidal monodispersed fine particles made by sol–gel make it possible to tailor all kinds of pore sizes, in a range which goes from a few nm to a few μm. An example of feasible structures is illustrated in Fig. 10, where SiO_2 particles are linked by a polymeric SiO_2 gel. The sol–gel ceramics most extensively used for filtration are alumina, zirconia, silica and various binary compounds such as cordierite and mullite. Their applications concern gas separation (e.g. dehydrogenation, desulphurization), food and biotechnology, such as dairy products, fruit juices, protein concentration, fermented alcoholic beverages, also the filtration and treatment of water and waste water.

Ceramic membranes are more expensive than organic polymer membranes. On the other hand, they are stable at high temperature. They are incompressible and they can be loaded under a large transmembrane pressure. They are chemically stable, especially in organic solvents. They are not sensible to bacterial action. They do not age significantly, so their lifetime is long. They can also be submitted to repeated backflush cleaning and steam sterilization operations. Moreover, it is possible to use advantageously the electrochemical activity of sol–gel membranes, by selecting an appropriate pH in the influent, so as to avoid fouling. For instance, the filtering flux of SiO_2

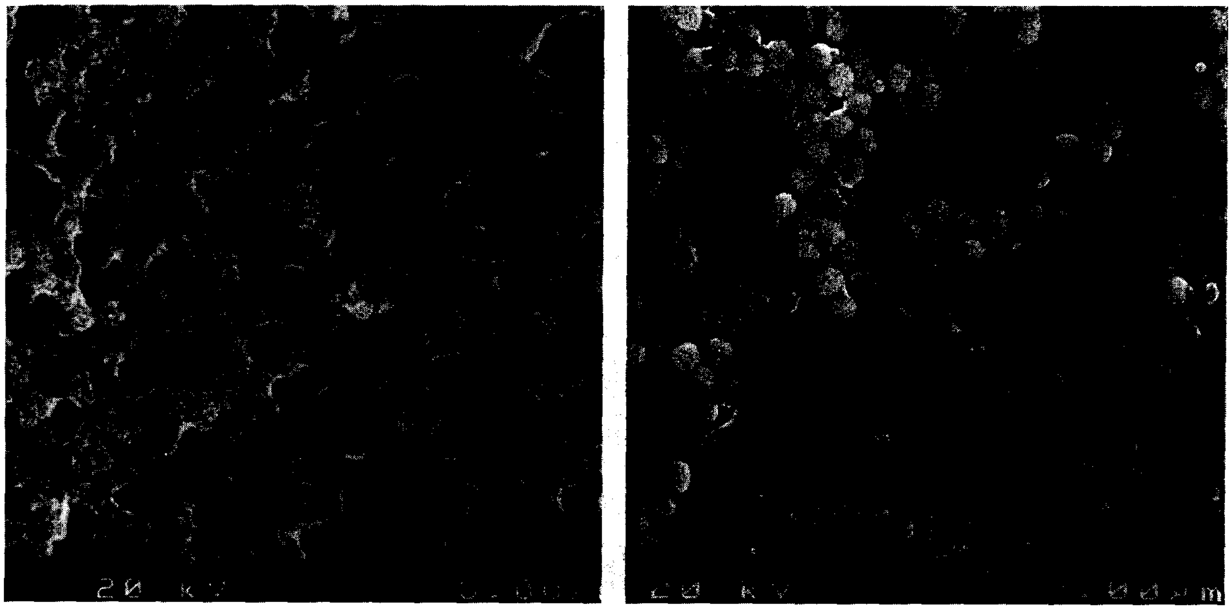


Fig. 10. SiO_2 porous network.

suspensions by Al_2O_3 membranes is low near the isoelectric point of Al_2O_3 (pH =9), while it is higher near the isoelectric point of SiO_2 (pH =2.5).[32]

Sol–gel ceramic membranes have such a high specific surface that they can combine catalytic properties with filtration properties. The catalytic activity can come from the ceramic itself, or from additives such as Fe, V or Cu. The additive can be placed inside the membrane by sol–gel or by infiltration with a liquid medium, or on top of the membrane (Fig. 11).

An important application of aerogels is in catalysis. They can provide porous supports for active catalytic materials, such as the noble metals (Pt, Pd, Rh, Ru).[6] They can also provide active catalytic phases (such as some perovskites) to replace the expensive noble metals. The main qualities of a catalyst are[33] its activity (% of a transformation achieved), selectivity (nature of the compound produced), durability, high specific surface area, high initial dispersion of the active phase, high thermal stability of the active phase, resistance to poisoning and macropores to allow easy access to the active sites. Xerogels are often microporous, they have a Langmuir type nitrogen adsorption isotherm. On the other hand, aerogels have meso- and macropores. They often have a better selectivity and activity than xerogels, due to a larger number of active sites, though this is not a general rule. For instance, $ZrO_2–SO_4^{2-}$ superacids, stronger than H_2SO_4, can be made by gelation of ZrO_2 with H_2SO_4. These gels are outstanding in catalysing the isomerization of normal paraffin into branched ones, which is an important process in petroleum industries.[33]

The applications of gels, and especially aerogels, in catalysis were extensively reviewed by Pajonk[23] and by Ward and Ko.[34] These applications can be divided into two domains: the production of high value organic compounds, and the protection of environment.

In the first case, the operation temperature is ≈400 °C, in conditions where aerogels keep a high specific area. Many synthesis reactions are concerned,[23] in particular partial oxidation, nitroxidation or hydrogenation of hydrocarbons. Monocomponent aerogels (SiO_2, Al_2O_3, ZrO_2, TiO_2, ThO_2, Cr_2O_3, Fe_2O_3, MoO_2) are very efficient as supports of catalyst as they enhance the activity. Many binary oxide aerogels, such as $NiO–Al_2O_3$, $V_2O_5–MgO$, $CuO–Al_2O_3$, or ternary oxide aerogels, such as $Cr_2O_3–Fe_2O_3–Al_2O_3$, were also developed. The active phase can be directly incorporated by sol–gel in the material, because oxides such as NiO, CuO, PbO and V_2O_5 are reduced in alcoholic medium during hypercritical drying, and they directly produce finely divided metal particles. These aerogels can be used as flow-through fluid beds.

In the second case, operation temperatures of 900–1200 °C, or possibly higher, are required, and most aerogels have a strong tendency to densify. The chemical reactions concerned are the transformation of the NO_x compounds to N_2, the clean combustion of hydrocarbons, to only reject CO_2 and H_2O in air, the simultaneous elimination of CO, NO_x and hydrocarbons from the exhaust gas of car engines. For this application, the $BaAl_{12}O_{19}$ compound mentioned previously, with a specific surface area of the order of 50 m^2/g at 1200 °C, seems to be very efficient.[35]

5 CONCLUSION

Ceramics with a large variety of different pore networks can be designed for different applications. The architecture of a porous network can be modified through the sol–gel chemical process and through the ceramics' heat treatment processing. A better control in the design of these porous networks will largely benefit from understanding how the general topology of a network, such as a fractal network, is modified during sintering. It is therefore expected that this branch of ceramics processing will see many interesting developments in the future.

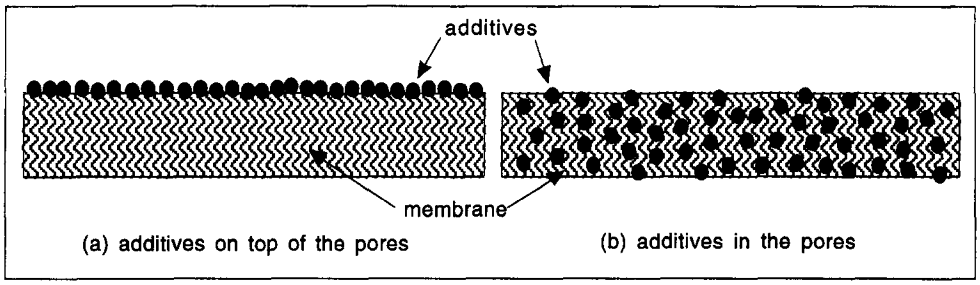


Fig. 11. Possible structures of modified ultrafiltration membranes.

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