Micro, Meso and Macroporous Inorganic Materials

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This work briefly reviews some recent advances in the field of micro- meso- and macroporous oxide materials, with applications ranging from catalysis to optical device construction. Zeolitic microporous material are first introduced, with a focus on their role in nanotechnology. Mesoporous silicate materials are then described. Not only their synthesis is achieved through the self-assembling of surfactant templates, but in addition to their application in catalysis, they can be used as confinement media in order to obtain new materials. Finally, we describe how a microscopic "lost-wax" approach can be used to fabricate oriented colloidal crystals. We stress the point that all these materials are typical nanotechnology products but they are obtained with typical chemical methods.

In recent years, new fields are developing along the borderline between chemistry and physics which are classified as belonging to "materials science" or to "materials chemistry and physics". In this article we briefly review the results obtained in one of these borderline fields, where the gradual change from chemistry to physics (in terms of concepts and applications) seems to be particularly evident and where a clear cut between the two disciplines is not possible or even completely inappropriate.

Zeolites and other microporous materials

Strictly speaking the term zeolites denotes a class of highly crystalline aluminosilicates, described by the general formula $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]^{x-}\cdot zH_2O$ (where M is a metal cation, a proton or, less frequently, a charged molecule) and having as characteristic feature a *three-dimensional*, *regular* array of intracrystalline nano-voids. The same term is however often used also with reference to nano-porous solids con-

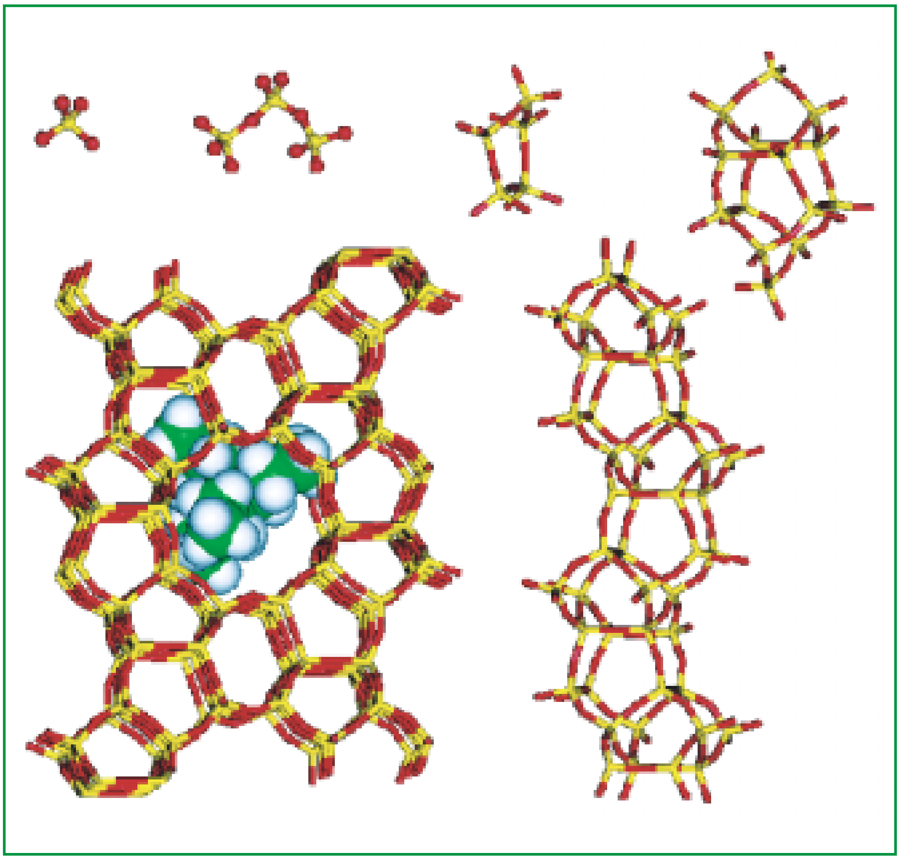

Figure 1 - Construction of the MFI framework of ZSM-5 zeolite starting from TO_4 primary units (T atoms, either Si or Al, are in yellow; O atoms in red). An encapsulated TPA^+ (tetra-propylammonium) ion is also shown, used as templating agent during the zeolite synthesis and acting as extraframework counterion balancing the negative charge of the framework

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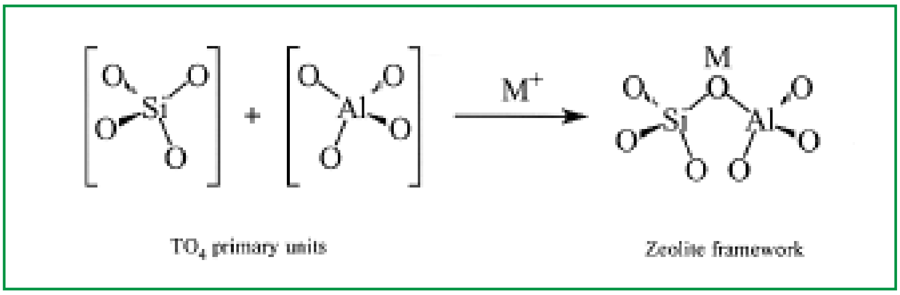


Scheme 1

taining elements other than Al (for instance P, Ti, Fe, Ga), which should be more properly classified as zeolitic or zeotype materials.

In this section, the structure of these solids will be illustrated at an elementary level only, mainly in view of the discussion of their interest in the field of nanotechnology. For more exhaustive structural information the reader is referred to more specialised papers [1,2] and to the atlas [3] published by the Structure Commission of the International Zeolite Association (IZA-SC) (also available at the website http://www.iza-structure.org/).

Every zeolite framework can be constructed starting from tetrahedral TO_4 primary units, where T=Si or a tetrahedrally coordinated atom substituting silicon (for instance Al), which are interconnected by sharing bridging oxygen atoms as schematically depicted in Scheme 1. It is most noticeable that, while the SiO_4 unit is neutral, TO_4 blocks containing elements T other than Si (for instance Al) can carry a net formal charge (-1) which must be balanced by a positive counterion (M^+ in Scheme 1) in order to ensure electrical neutrality. Upon interconnection of the TO_4 building blocks a variety of three-dimensional structures can be obtained, all characterised by extensive internal porosity. To illustrate this point, the construction of the MFI (following the IZA-SC nomenclature) framework is depicted in detail in Figure 1. This structure is typical of silicalite and ZSM-5 zeolites and of zeotype materials like Fe- and Ti-silicalite. The internal porosity arises from the presence of well shaped channels, the largest ones being delimited by 10 TO_4 units or, alternatively, O atoms.

The type of framework is actually obtained by interconnection of the TO_4 primary units and, as a consequence, the geometry, dimension and distribution of the internal voids depend on both the preparative *(zeolitization)* conditions and the Si/Al ratio [4]. As the latter can in principle assume any value between 1 (lower limit found in zeolite X) and infinity (as found in silicalite and siliceous FER), this accounts for the large, continuously growing number of known zeolitic structures. Some of the most common structures are shown in Figure 2.

The presence of extra-framework counterions is needed when substitution of framework silicon with an heteroatom results in the appearance of a net charge (as in the case of Al). The possible occupancy of such ions in mordenite (MOR), MFI (ZSM-5) and BEA (Zeolite Beta) structures (all characterised by an internal porosity arising from a system of channels) is illustrated in Figure 3 (data from ref. [5]). Based on Figures 1-3 we can now better describe some of the distinctive features of zeolites and zeotypes. In particular:

1) the intra-crystalline voids can assume the shape of cages, channels or pockets with dimension in the nanometre range. It is noticeable that these voids can be accessible to molecules of appropriate size and shape through apertures of well defined dimensions, the most common being constituted by rings consisting of 8, 10 or 12 oxygen atoms (with corresponding pore openings of about 0.4, 0.55 and 0.73 nm in size respectively). Because of this intrinsic porosity zeolites are excellent materials to be used as adsorbent, molecular sieves, and shape selective catalysts;

2) the charge-balancing extra-framework cations occupy well defined crystallographic positions. It is noticeable that these ions are exposed at the surface of the intracrystalline cages and channels where they can act as Lewis acid centres (as also do structural defects and extraframework aggregates). These extra-framework cations, which can be easily exchanged, are the main source of intrazeolite electric fields, whose strength depends on the cation radius and charge. Their Lewis properties and the electrostatic fields they generate render the counterions capable of forming adducts with molecules moving inside the framework; this interaction can sometime result in a strong electronic perturbation of the adsorbed molecules and finally in their chemical activation. The zeolitic cavities can therefore act as shape selective nanoreactors, the shape selectivity being determined by the spatial restrictions imposed by the geometry of the voids, where the active centres (usually extraframework cations) are exposed. In this respect, the analogies with enzymatic systems are noteworthy. The case of protons acting as counterion deserves some further comment. In proton-exchanged zeolites bridging Si(OH)Al groups are in fact present which confer a remarkable Brønsted acidity to the framework. These species can form hydrogen bonded adducts with molecules entrapped inside the zeolite voids which, in proper conditions, can further evolve towards protonated species. Formation of hydrogen-bonded precursors and protonation are usually the first stages of Brønsted acid-catalised reac-

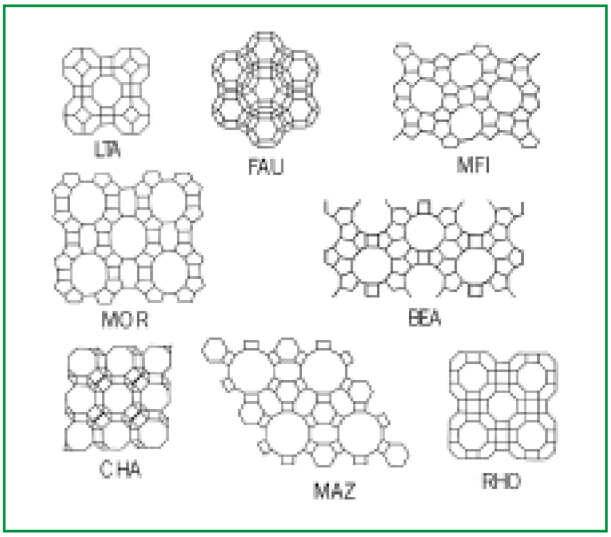


Figure 2 - Schematic representation of some zeolitic frameworks. The positions of the oxygen atoms are omitted. The straight segments connect the positions occupied by the T centres of the TO_4 tetrahedron

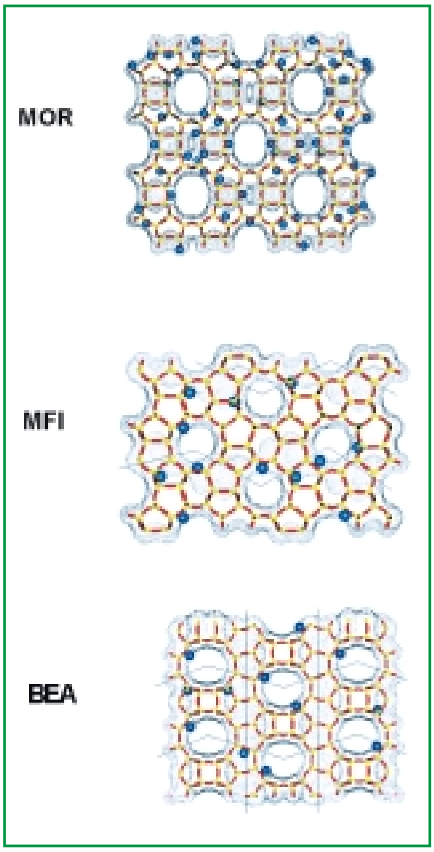


Figure 3 - Possible occupancy of the extraframework counterions (blue spheres) counterbalancing the framework negative charge in MOR, MFI, and BEA zeolites. The dotted portions evidence the internal spaces not accessible to molecules. The black lines are the traces of channels running parallel to the figure plane

tions, which together with shape-selectivity, make zeolites heterogeneous catalysts of paramount importance in petrochemistry.

Zeolites and other microporous materials as templates for obtaining organic replicas and nanostructured carbon

Zeolites and zeotype materials described in the previous section can be used to obtain microporous organic and inorganic replicas whose structure is shaped by that of the nanovoids of the templating material.

An example of a micropore filling procedure making use of classical nanotechnological procedure (molecule by molecule) is the formation of acetylene, ethylene, propylene, pyrrole, thiophene etc. polymers into the channels of ZSM5. The polymerization inside the channels is catalyzed by the strong Brønsted acidity. As for acetylene is concerned the intra-cavity polymerization follows the path showed in Scheme 2.

The colored, positively charged polymer gradually fill the internal voids with formation of a complex tridimensional structure replicating the shape of the channels. The same happens with ethene and other monomers. As the polymeric species are resistant to the attack of HF solutions, which on the contrary dissolve the siliceous framework, organic replicas can be obtained with this method, provided that the polymer network can withstand the loss of the matrix, i.e. it is sufficiently interconnected.

Zeolites can be used also to obtain pure carbon replicas *via* acid catalyzed internal polymerization and successive pyrolisis of furfuryl alcohol [6] followed by dissolution of the siliceous framework with HF solution.

Inorganic nanostructured replicas of zeolites and zeotypes could, in principle, also be obtained in this way. However this route has not been yet intensively investigated.

Mesoporous oxidic materials (from MCM41 to aerogels)

While the pores diameters in zeolites and zeotypes is below 1.5 nm, the diameter of the pores of mesoporous molecular sieves is in the 2-10 nm range.

Mesoporous molecular sieves can be prepared starting from a silica source using alkylammonium surfactants with chains longer than those used in the synthesis of zeolites (for a review see ref. [7]). In this case the templating entities are surfactant micelles like those represented in Figure 4.

As the diameter of the micelles is depending on the length of the hydrocarbon chain, it is evident that this method allows to synthesize in a controlled way a variety of mesoporous molecular sieves characterized by pore diameters comprised in a wide range. Once the organic templating agent is eliminated by means of calcination, a mesoporous material is obtained with molecular sieving properties. The exagonal regular arrangement of the channels is well evident in Figure 5, where the structure of MCM41 molecular sieve is represented.

These materials find applications not only in the traditional field of catalysis and sieving but also for quantum confinement, synthesis of molecular wires, i.e. the classical fields of nanotechnology. In other words we are in presence of a material with both chemical and physical applications.

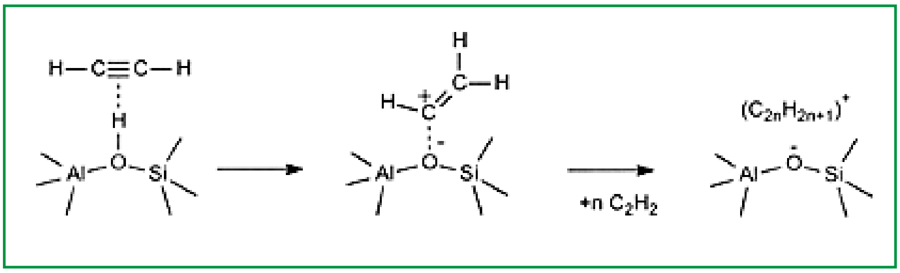
The pore structure of aerogels is formed by the controlled condensation of small (polimeric or colloidal) primary particles with diameter of 1-3 nm [8]. They are fully amorphous and their solid content is only 10-15% vol. For this reason they are extremely good thermal insulators. A schematic representation of the structure of these solids is reported in Figure 6.

These solids find applications not only as thermal insulators but also as catalysts support or in other more exotic applications (for instance for collecting cosmic dust). Carbon aerogels can find applications as electrode materials because of their low electric resistance, their controlled pore-radii distribution (1-50 nm) and their high specific surface area. Also in this case we are dealing with materials with both chemical and physical applications.

Macroporous oxides

Synthetic opals and similar materials

As briefly mentioned in the previous paragraphs, microporous and mesoporous materials are prepared by crystallization around small molecules (zeolites and zeolitic materials) or condensation around supramolecular aggregates of surfactant molecules (mesoporous molecular sieves like MCM 41). However the size of the pores is limited to the



Scheme 2

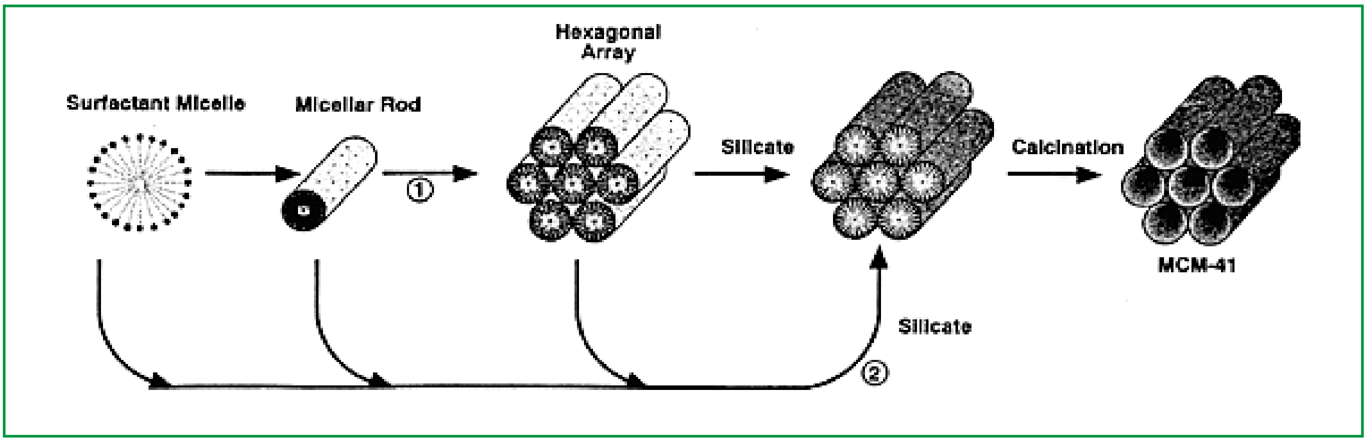


Figure 4 - A schematic representation of surfactant templating

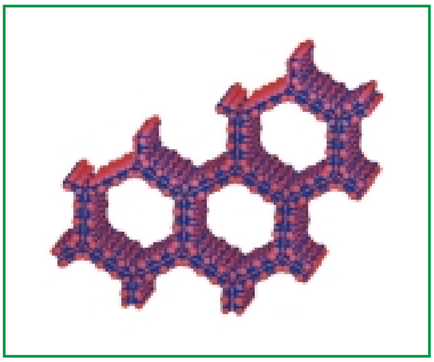


Figure 5 - A model of the structure of MCM-41. Silicate walls are amorphous, but arranged in a regular array

dimensions of the organic templates (from 3 to 10 nm).

Inorganic materials with much wider pores in the size range of hundredths of manometers to micrometers could be of wide interest for many (non catalytic or adsorptive) applications. So the problem of their synthesis has attracted the attention of many researchers.

To exemplify the problems encountered in the synthesis procedure it is probably useful to illustrate in simple terms what we mean with "macroporous solids".

Let us assume for simplicity that these solids can be represented as constituted by a tridimensional collection of individual particles: for instance metal oxide particles with spherical shape and about 50 nm average diameter, brought together by compression. If the diameter of the individual particles is spread on a wide interval, their condensation by compression, sedimentation or any other process, originates a disordered solid and the voids between the particles have dimensions also spread over a wide interval (wide pore distribution). In the so formed solid, where the individual particles are bound by physical forces, no spatial regularity exists, either with short range or long range character. These solids are fully amorphous. A situation of this type is encountered for example when polydispersed silica particles are compressed under high pressure. If the sample is treated at high enough temperature to induce some sintering with formation of interparticles chemical links through SiOSi bridges, a stable rigid solid can be obtained. Its high surface area and wide pore distribution make this material similar to other monolithic silicate materials like Vycor glass or silica xerogels. The situation is similar to that represented schematically in Figure 7a.

On the contrary, if the individual particles are monodispersed, the resulting situation after compression or sedimentation can be entirely different. In fact (Figure 7b) the microspheres can, in principle, pack together in a regular array. That this is the case has been first demonstrated by K. Osero-Asare and F.J. Arriagada [9] and developed by Stacey A. Johnson *et al.* [10]. The regular arrangement of the spheres in these solids, representing a synthetic analogue of natural opals, confers them interesting physical properties. Synthetic opals are obtained also in several other ways which cannot be reviewed here for reasons of brevity (we refer the reader to ref. [11] for more information). Let us illustrate the reasons why these type of solids are so interesting. It is sufficient to recall that in a solid constituted by a tridimensional periodic arrangement of particles, we are in presence of a periodic modulation of the dielectric constant. Yablonovicth [12] and John [13] have shown that if the modulation has a spatial periodicity of the same length scale of the electromagnetic radiation in which the solid is immersed (e.g. optical wavelengths), electromagnetic waves behave in a manner similar to electrons in a crystal. An optical band gap (i.e. a prohibited wavelength gap) can appear,

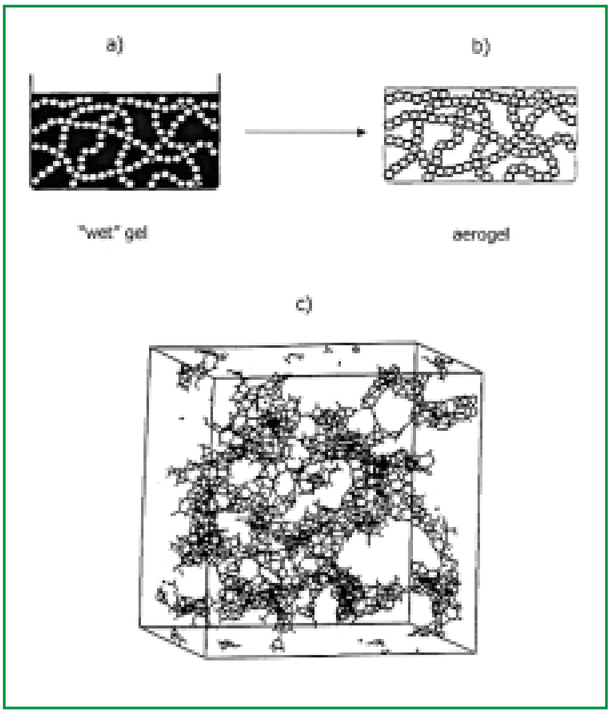


Figure 6 - Models of aerogel structures (adapted from ref. [8]): a) wet gel (dark is liquid); b) dry aerogel; c) an atomistic model of silica aerogel

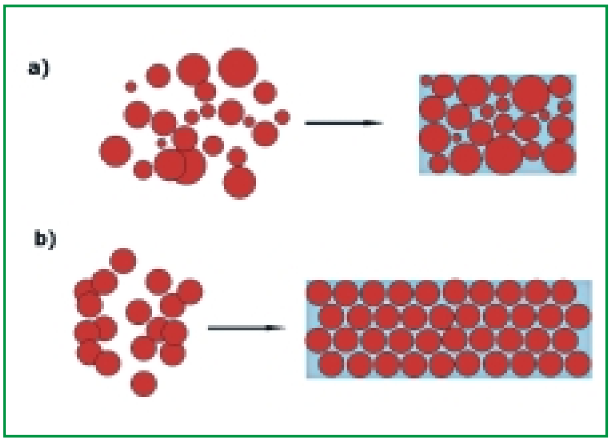


Figure 7 - A schematic representation of self assembling in spheroidal powders: a) polydisperse particles form amorphous aggregates; b) monodisperse particles form colloidal crystals

analogous to the electronic band gap of semiconductors. This quality allows the confinement and control of electromagnetic waves in the crystal, and the materials where these effects take place are called "photonic".

For instance they can be used as filters, mirrors, optical cavities and waveguides. Moreover, it has been proposed that they can be used to create a new family of light-emitting devices, in which the photonic effect tunes the emission of excited chromophores located in the porosity itself.

As, in principle, similar solids can be made also by using TiO_2 and Al_2O_3 spheroidal particles, it follows that this field has a broad potentiality in terms of practical applications.

Inverse opals and other template macroporous materials

A way to create periodic oscillations of the type illustrated before in a siliceous material, is to fill the voids of a colloidal crystal formed by spheres of an organic material with silica, or any other oxidic material, and then to remove the polymer by pyrolysis [14]. In this way a large variety of solids named "inverse opals" are obtained, which greatly expand the number of photonic macroporous solids which can be successfully synthesized. Also in this case the applications in the field of photonics are prevailing.

The synthesis of macroporous systems by means of the lost-wax method

This method is based on the use of high quality colloidal crystals to create polymeric templates for the formation of a second generation of colloidal particles which can be constituted by silica or by any other oxide [15]. Examples of this type of are the colloidal crystals of TiO_2, ZrO_2-Al_2O_3, Al_2O_3 constituted by spherical or ellipsoid particles. The ellipsoid shape of the particles can be the result of appropriate deformation of the polymer template following the scheme presented in Figure 8 [16].

It is evident that this two stage replication process associated with intermediate stretching of the polymer template allows, in principle, to prepare a new generation of colloidal crystals where not only the diameter but also the shape of the particles can be controlled in a reproducible way. This result should further increase the possibilities of modulation of the optical properties of the colloidal crystals, increasing their potentialities in the construction of photonic devices.

Conclusions

Porous solids characterized by pore diameters ranging from about half to about one hundred manometers form a family of materials whose properties are gradually influenced by the pore dimensions. In fact we are moving from materials having mainly chemical applications in catalysis, separation and adsorption (zeolites and microporous materials) to materials with both chemical and physical applications (mesoporous materials) and to materials having preferentially physical applications (macroporous materials). All these have a common character: they are typical nanotechnology products, but they can be synthesized with chemical methodologies. These solids allow nanometric synthesis and manipulation of molecules (sieving and catalysis), confinement of new nanostructures (quantum dots and quantum wires) and confinement of electromagnetic waves (optical applications).

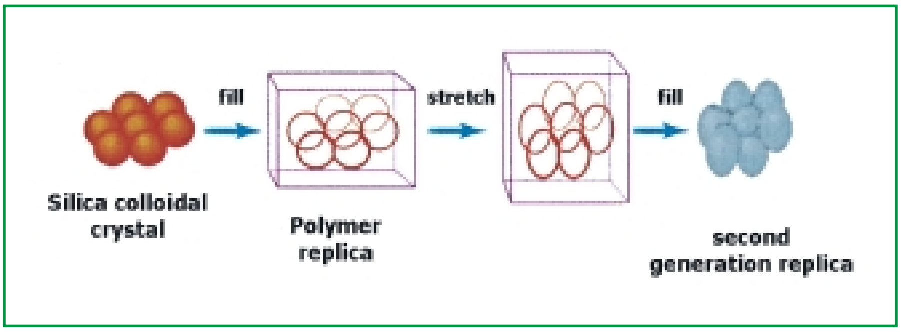


Figure 8 - The lost-wax approach for the fabrication of macroporous oxide structures

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