

## Tailoring of Ceramic Porosity by Templating Effect

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### INTRODUCTION

The porosity of a ceramic material can be tailored by incorporation of templating units during their synthesis. These templates can be further removed to generate corresponding pores in the final materials. The choice of the removable units depends on the required pore size and shape. They can be small individual organic, inorganic or metal-organic molecules, molecular aggregates like lyotropic liquid crystal phases, organic polymers or solid particles.

This paper will describe various examples of synthesis of mesoporous (pore size between 50 nm and 2 nm) or microporous materials (pore size less than 2 nm) by the templating effect. It must be, however, noted that this way of synthesis can also be applied to the preparation of macroporous materials (pore size greater than 50 nm) like for instance ceramic filters by casting ceramic slurries into polymeric foams or silica layers from a mixed suspension of colloidal silica and organic latex.<sup>1</sup>

The removal of the templating unit can be carried out by a wet chemical or a thermal way with or without decomposition of the template. This elimination stage induces some limitation concerning the size of the feasible ceramic bodies. The mesoporous and microporous materials exhibit a low permeability. A uniform removal of the templates without collapse of the solid part can be easily obtained in the case of small grains produced by hydrothermal synthesis or for continuous thin layers derived from the sol-gel route.

Another feature of the process concerns the ability of the templating species to direct the struc-

ture of the inorganic network in order to prepare final materials exhibiting an ordered porosity with well defined pore sizes and a controlled connectivity of the porous and solid parts.

### TEMPLATING WITHOUT STRUCTURE DIRECTING EFFECT ON THE INORGANIC NETWORK

This way of synthesis was recently studied in the case of oxide ceramics prepared by the sol-gel route from the hydrolysis and condensation of alkoxide precursors,  $M(OR)_n$ . Two strategies are applied;

- in the first route, templating molecules are incorporated in the gelation medium, which are inert towards the chemical process leading to the inorganic network. (route (c)-(d) on Fig. 1);

- for the second strategy, chemically modified alkoxides are used. A molecular group acting as template is grafted on the precursor before the polymerisation stage. This way of synthesis is also schematically represented on Fig. 1 (route (a)-(b)-(d)).

The synthesis conditions are always selected in order to directly associate the porosity in the final material to the departure of the templating species during the stage (d).

A first example related to the first strategy is a work on microporous silica layers prepared by hydrolysis and condensation of silicon alkoxide in the presence of organic molecules.<sup>2</sup> These molecules are non-ionic surfactants and more precisely octyl aryl polyether alcohols with a general formula  $C_8H_{17}-C_6H_4-(OCH_2CH_2)_x-OH$  where  $x=1,3,9$ ,

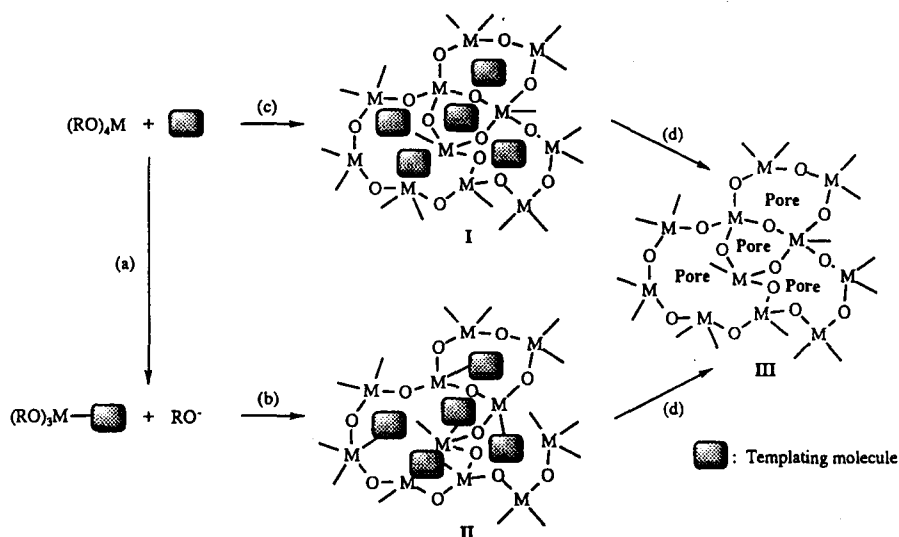
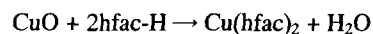


Fig. 1. Schematic illustration of the organic/inorganic template strategies. (from ref. 2)

10 or 30. The porous characteristics of the materials after a thermal treatment up to 450 °C were determined by nitrogen adsorption and are reported in Table 1. While the materials synthesized without surfactant additives do not exhibit any measurable porosity by nitrogen adsorption, the results of Table 1 show clearly that both the porous volume and the micropore size can be tailored by both the added amount of surfactant and the length of the polyoxyethylene chain.

Another example associated to the first strategy concerns the preparation of porous silica using inorganic templating species.<sup>3</sup> A volatile inorganic compound, copper hexafluoroacetylacetonate Cu (hfac)<sub>2</sub> can be used which does not react with the growing silica polymers produced from tetraethoxysilane (Si(OEt)<sub>4</sub>). In another case, a mixed oxide

is firstly synthesized from molecular precursors Si (OEt)<sub>4</sub> and Cu(OCH<sub>2</sub>CH(CH<sub>3</sub>)N(CH<sub>3</sub>)H)<sub>2</sub> and then dry or wet etched by hexafluoroacetylacetonate. This etching process induces the removal of the copper oxide from the inorganic network according to the following reaction:



In Table 2 are reported the textural properties of the various final materials.

The second way of synthesis consisting of the chemical modification of the alkoxide precursor can be illustrated by the two following examples;

- the preparation of various microporous or mesoporous oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, and SnO<sub>2</sub>) from hybrid precursors obtained by reaction of an alkoxide with polyacrylic acid (Mw=2,000) followed by the

Table 1. Effect of surfactant size and concentration on the porous texture of the resulting silica layers. (from ref. 3)

x	Surfactant /TEOS molar ratio	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Porous volume (cm <sup>3</sup> g <sup>-1</sup> )		Porosity (%)	Hydraulic pore	
			total	microporous		range	mean
1	0.55	400	0.217	0.210	32.2	3-7	3.9
3	0.16	250	0.121	0.105	20.9	3-6	3.2
3	0.35	470	0.197	0.190	30.1	3-6	3.4
3	0.55	500	0.249	0.239	35.5	3-6	3.7
10	0.55	728	0.510	0.480	52.7	5-9	6.3
30	0.55	800	0.541	0.514	54.2	4-10	6.0

Table 2. Porous texture of mixed oxides Cu(II)/SiO<sub>2</sub>. (from ref. 2)

System	Treatment	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Average pore radius (Å)
SiO <sub>2</sub> /Cu oxide (2:1)	hydrolysed	2	11
SiO <sub>2</sub> /Cu oxide (4:1)	hydrolysed	187	11
SiO <sub>2</sub> /Cu oxide (9:1)	hydrolysed	279	107
SiO <sub>2</sub> /Cu oxide (2:1)	dry etched	11	44
SiO <sub>2</sub> /Cu oxide (4:1)	dry etched	588	10
SiO <sub>2</sub> /Cu oxide (9:1)	dry etched	515	73
SiO <sub>2</sub> /Cu oxide (2:1)	wet etched	15	126
SiO <sub>2</sub> /Cu oxide (9:1)	wet etched	429	77
SiO <sub>2</sub> /Cu(hfac) <sub>2</sub> (4:1)	as prepared	187	11
SiO <sub>2</sub> /Cu(hfac) <sub>2</sub> (4:1)	110 °C in vacuo	588	10

thermal elimination of the polyacrylate groups which are present in the dried gel<sup>4</sup>;

– the synthesis of mesoporous silica from modified silicon alkoxides exhibiting two or more ending groups (RO)<sub>3</sub>Si- bonded to a purely organic chain by Si-C bonds<sup>5</sup>. These precursors are more precisely alkoxyxilanes containing mono or diyne units. After polymerisation of the solutions by hydrolysis and condensation of the terminal alkoxy groups, the resulting gels are immersed in an aqueous solution containing fluoride ions. The Si-C bonds are preferentially cleaved and the organic part is extracted by the aqueous solution. After drying and thermal treatment, the diameter of the created mesopores ranges from 1.5 to 7 nm. This diameter depends on the size of the initial organic part of the hybrid precursor but is clearly larger.

#### TEMPLATING WITH STRUCTURE DIRECTING EFFECT ON THE INORGANIC NETWORK

In that case, the templating units orientate the growth of the inorganic network and leads to the formation of ordered structure and porosity. The periodicity of the structures involves the pore size monodispersion and defines a uniform connectivity of the porous and solid networks.<sup>6</sup>

#### Use of individual molecules-preparation of molecular sieves

Microporous solids exhibiting a structural porosity are usually obtained by hydrothermal synthesis

using a small molecule as a template.

The zeolites constitute the main family of these microporous materials<sup>7</sup>. Examples of zeolites structures are given on Fig. 2. Their synthesis is carried out by thermal treatment of aluminosilicate gels in

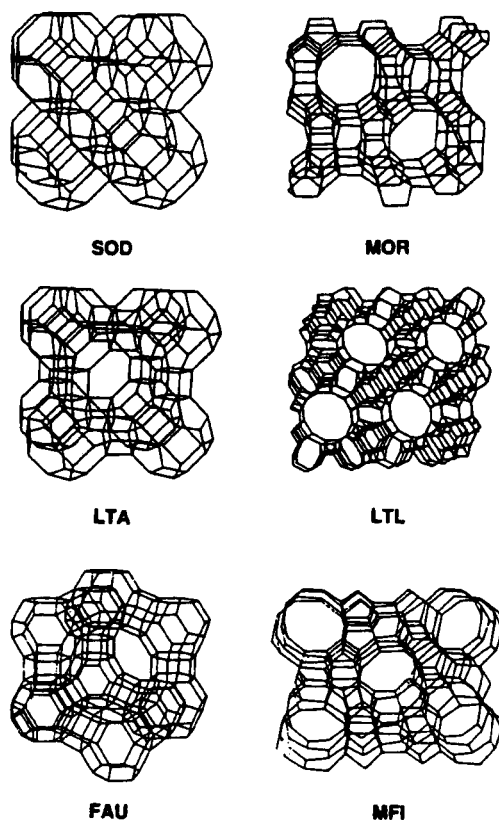


Fig. 2. Main zeolite structures. (from ref. 8) SOD: sodalite; LTA: Linde type A zeolite; FAU: faujasite-zeolites Xor Y; MOR: mordenite; LTL: Linde type L zeolite; MFI: ZSM-5.

a basic aqueous medium in presence of a templating molecule. This molecule is often a tetrasubstituted quaternary ammonium as for instance tetrapropyl ammonium. Substitutions of aluminium or silicon by other elements are possible and pure silica structures like silicalite<sup>9</sup> can also be obtained. The hydrothermal treatment produces crystallites with a usual size in the micrometer range. The thermal elimination of the template gives rise to cavities with a maximal diameter close to one nanometer connected by windows smaller than 0.7 nm which is the upper limit of the ultramicroporosity.

Molecular sieves with a larger porosity are aluminophosphate or gallophosphate compounds like cloverite.<sup>10</sup> The potential diameter of their cavities and windows are respectively equal to 3 nm and 1.3 nm. These solids are obtained by hydrothermal synthesis in neutral or slightly acidic aqueous medium in presence of an amine acting as template unit. Oxyfluorinated microporous solids can also be prepared.<sup>11</sup>

Various models were proposed in order to explain the structure directing effect of the template molecules on the growing zeolite structure. A schematic representation of the C or "can and cement" model<sup>12</sup> is given on Fig. 3.

#### Use of mesophases of lyotropic liquid crystal type

The main lyotropic liquid crystal are lamellar, hexagonal and cubic phases (Fig. 4). They are obtained by a self-assembly process of surfactant molecules for intermediate compositions in the

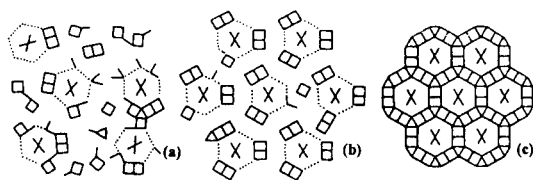


Fig. 3. Schematic drawing of the first stages of growth of nuclei according to the C model. (from ref. 12) (a) An early stage of the reaction mixture or gel. "X cans" are water clusters with or without inorganic ions or charged template molecules. A hypothetical domain of influence is dotted. The building units are depicted by squares, triangles and bars. (b) Mutual repulsion among the X units causes an order. (c) A framework ("cement") is built between the X units.

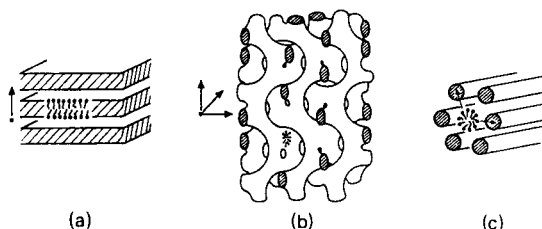


Fig. 4. Drawing of three lyotropic liquid crystal structures (from ref. 13): (a) lamellar, (b) bicontinuous cubic (space group Ia3d) viewed along  $\langle 100 \rangle$  direction, (c) hexagonal.

water-surfactant binary diagrams. The sizes of the constituting units, i.e. the amphiphilic aggregates are usually ranging from 2 to 10 nm. So it seems very attractive to use these mesophases as growth medium for inorganic networks in order to prepare new materials with an ordered porosity in the range of the supermicroporosity ( $> 0.7$  nm) or mesoporosity ( $> 2$  nm).

It must be noted that this way of synthesis can be associated to natural synthesis processes of biomineralization. There is currently a considerable interest in this new field of material science related to a biomimetic approach and to the concept of nanochemistry.

Some examples will be now described dealing with the synthesis of porous oxides using liquid crystal templating effects. These examples will differ by the process of formation of the oxide network.

**Hydrothermal synthesis-mesoporous molecular sieves M41S.** In 1992 researchers at Mobil published a synthesis method of mesoporous molecular sieves using the templating effect of lyotropic liquid crystal mesophases.<sup>14-15</sup> The aluminosilicate or silicate materials labelled M41S, are prepared by hydrothermal treatment of solid or molecular precursors of alumina and silica in the presence of cationic surfactants of alkyl trimethyl ammonium halogenide type,  $C_xH_{2x+1}(CH_3)_3N^+X^-$  with  $x$  ranging between 8 and 16 carbon atoms. As in the case of zeolites, micrometer sized crystallites can be obtained and a firing treatment induces the removal of the surfactant aggregates and the appearance of the ordered porosity. The variation of the initial chem-

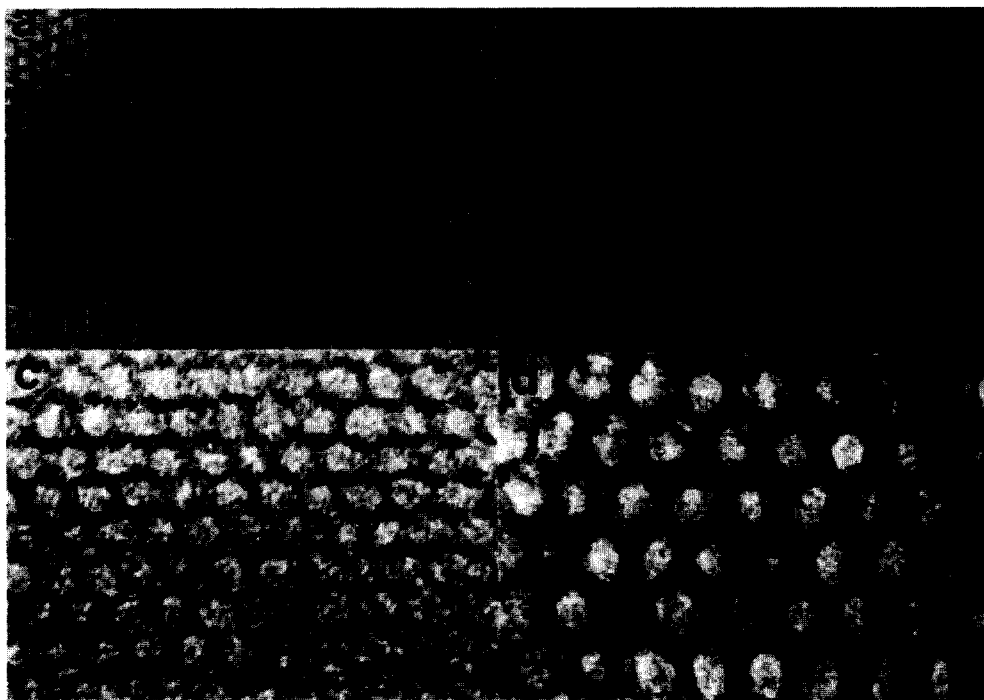


Fig. 5. Transmission electron microscope images of various MCM41 samples (from ref. 15)-pore size: (a) 2 nm; (b) 4 nm; (c) 6.5 nm; (d) 10 nm.

ical composition controls the structure of the formed mesophase: lamellar, hexagonal or cubic. The main material labelled MCM41 exhibits a hexagonal ordered porous texture with dimensions in good agreement with those observed for a pure water-surfactant hexagonal phase. The pore size is directly controlled by the length of the alkyl chain of the surfactant and is ranging between 1.8 and 10 nm (Fig. 5).

Different mechanisms were proposed to explain the synthesis of the MCM41 material (Fig. 6). The growth of the inorganic network could occur before or after the formation of the micellar cylinders and their close packing into hexagonal arrangements (Fig. 6(a) and 6(b)) or with the formation of an intermediate lamellar phase (Fig. 6(c)). Nevertheless the mechanisms of the oxide polymerisation and the mesophase formation are clearly co-operative. Monnier *et al.*<sup>17</sup> explained this co-operative process by the evolution of the coulombic type interactions which exist between the polar head of the surfactant molecules and the growing silicate oligomers.

#### Polymeric sol-gel synthesis of silica layers with an ordered microporosity.

Thin silica layers were obtained by the polymeric sol-gel route at room temperature.<sup>18-20</sup> The silica precursor is a silicon alkoxide which is mixed with an aqueous solution of cationic surfactant of alkyl trimethyl ammonium bromide type:  $C_xH_{2x+1}(CH_3)_3N^+Br^-$  ( $x=8, 10, 12$ , or  $14$ ). The corresponding composition is located in the isotropic area of the corresponding binary diagrams. The solution is initially fluid and thin layers are easily deposited. The gelation of the silica network and the mesophase formation are simultaneous. The wet gels exhibit a hexagonal structure for the lower values of  $x$  (8 and 10) and for higher values of  $x$  the wet gel is lamellar. This result can be correlated with the data reported on Fig. 6c. The retention of the ordered structure after firing is evidenced by X-ray diffraction (Fig. 7). That confirms clearly that the inorganic network is directly implied in the structure of the mesophase. The mesophase defines the organisation of the pores around the amorphous sil-

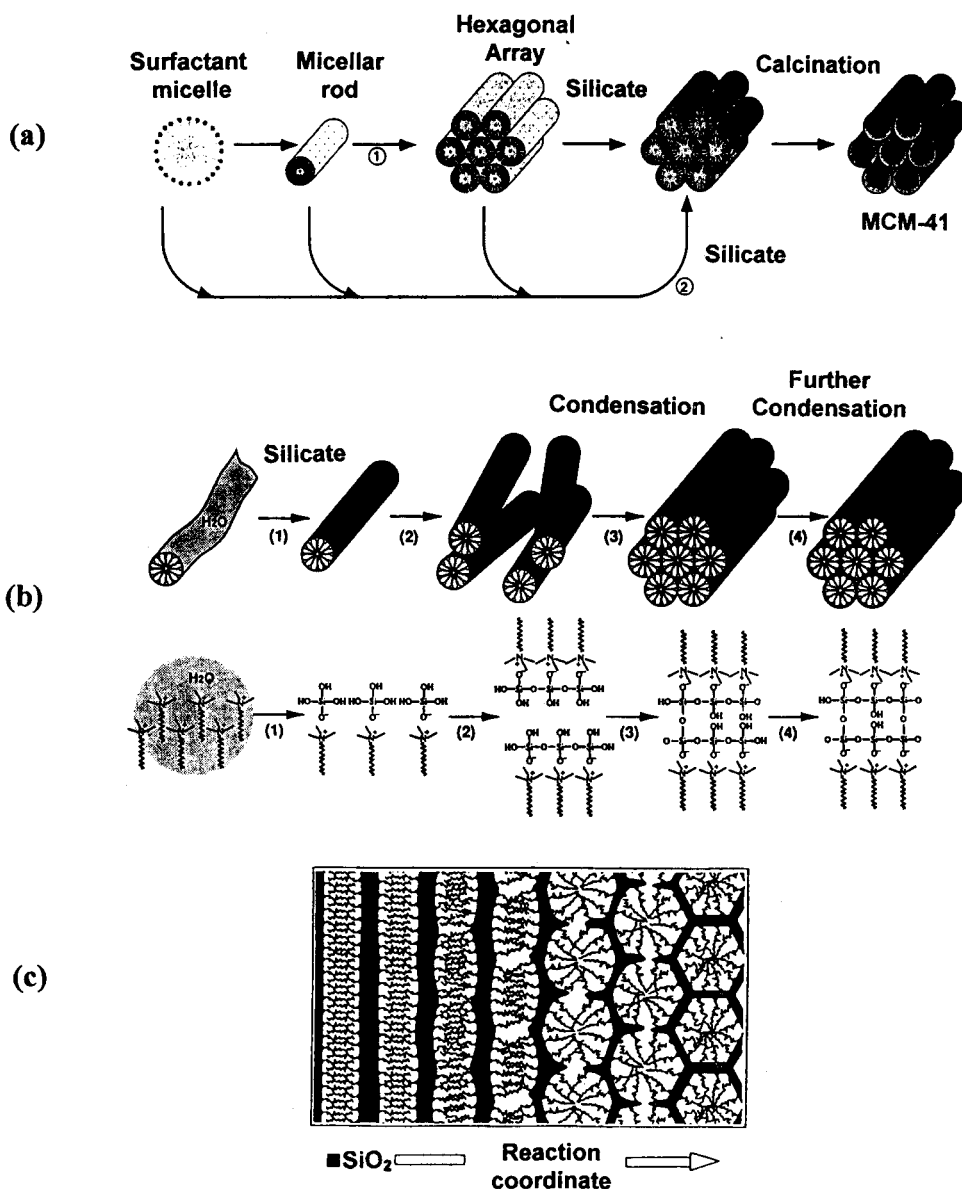


Fig. 6. Schematic representation for the formation process of the MCM 41 materials. a) from ref. 15; b) from ref. 16; c) formation of an intermediate lamellar phase during the co-operative process (from ref. 17).

ica network. The experimental study of the porosity by nitrogen adsorption confirms that the pore size in the final material is controlled by the characteristics of the structure directing mesophase (Fig. 8). These materials are very attractive candidates for applications in separative processes which require microporous membranes with cali-

brated pores.<sup>21</sup>

**Synthesis of mesoporous materials from a layered polysilicate<sup>22</sup>.** In that case, the template unit does not orientate the growth of the inorganic network but induces a strain in the initial layered structure (Fig. 9). The ordered mesoporous material is obtained by ion exchange of Na<sup>+</sup> ions of a

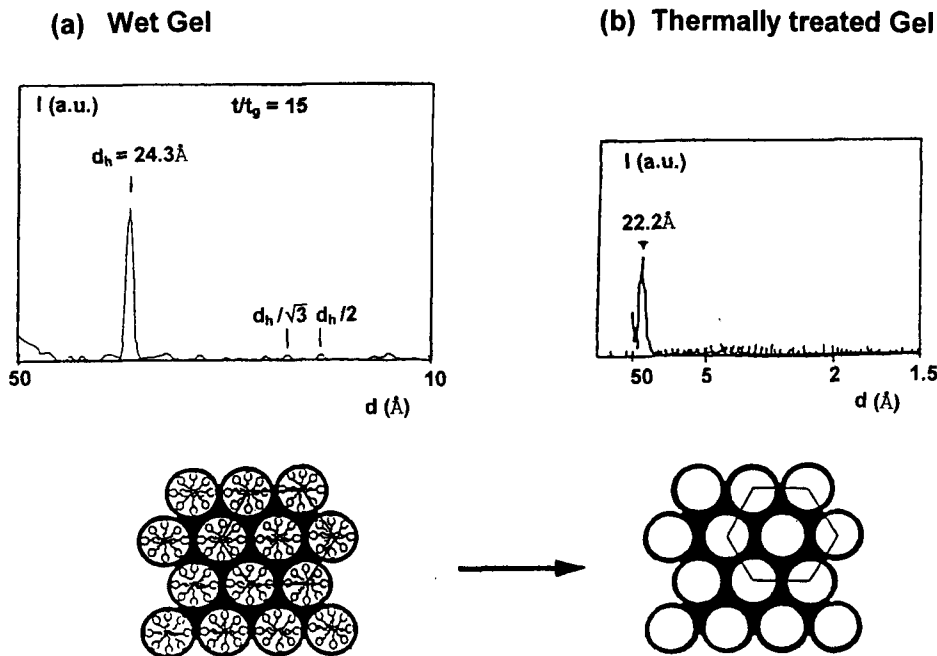


Fig. 7. Gel obtained with octyl trimethyl ammonium bromide ( $x=8$ ). a) X-ray pattern and schematic representation of the hexagonal structure for the wet gel; b) X-ray pattern and schematic representation of the structure for the thermally treated material.

layered polysilicate, kanemite ( $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ), by hexadecyltrimethyl ammonium ions,  $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3 \text{N}^+$ . This mechanism can be interpreted as an intercalation process of micellar cylinders. After firing the final particles exhibit clearly an ordered porosity.

**Synthesis of anisotropic crystalline alumina layers by a colloidal sol-gel route<sup>23</sup>.** A lamellar liquid crystal phase is used to direct the aggregation pro-

cess of colloidal alumina particles. An alumina hydrosol and cationic surfactants of  $\text{R}(\text{CH}_3)_3\text{N}^+\text{Br}^-$  type where R is a complex hydrophobic double chain are mixed. The lamellar structure is preserved after the departure of the surfactant above  $300^\circ\text{C}$  and also at higher temperature after the crystallisation of the oxide into an alumina (Fig. 10). This directed aggregation process could be favoured by the plate like shape of the colloidal particles of the starting hydrosol. This particular shape enables their insertion into the lamellar mesophase with geometrical distortion.

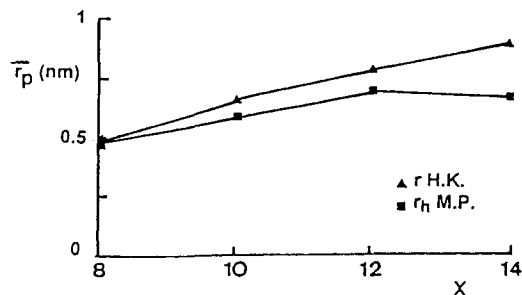


Fig. 8. Evolution of the pore size versus the length of the alkyl chain of the surfactant. Measurements using the MP or Horvath Kawazoe methods.

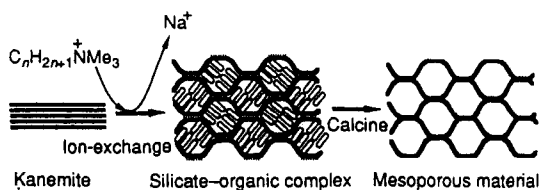


Fig. 9. Schematic representation for the formation of a mesoporous material from kanemite (from ref. 22).

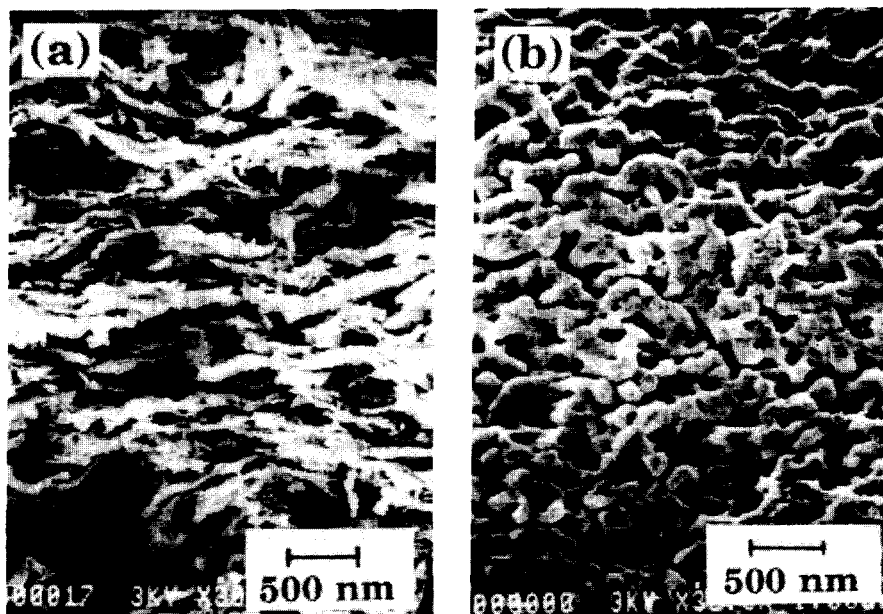


Fig. 10. Scanning electron microscope images of a alumina thin layers after firing at 1000 °C (from ref. 23) . Films prepared with (a) or without surfactant (b).

## CONCLUSION

The porosity of a ceramic material can be tailored using templating units during the synthesis. The final porosity is directly defined by the size and shape of the templating units. The templates can be individual molecules, aggregates or solid particles with or without structure directing effect on the inorganic network. Various examples from literature were given in this paper which illustrate the potentialities of this emerging area of research in ceramic material science. The specific properties of this type of material open the field to a wide range of applications such catalysis, membranes and sensors.

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