Unraveling the importance of zeolite crystal morphology

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Abstract	The design and control of chemical systems over multiple-length scales ranging from the molecule to the crystal represent one of the greatest challenges in science. The ability to understand how molecules organize to build superstructures which exhibit tailored properties is of prime importance. Zeolites are microporous crystalline aluminosilicates being both used in main petrochemical processes (cracking, alkylation, acylation, isomerization) and as a confinement medium for metal cations to perform bifunctional catalysis. The rational design of these inorganic polymers with highly crystalline structure is warranted to achieve a proper chemical composition, an appropriate crystal size and assembly along with hierarchical porosity. The challenges consist of properly tailoring zeolite catalytic properties (acidity, metal doping, particle size) for a targeted application and, if possible, predict their reactivity.
Keywords	**Zeolite, morphology, crystallization, hierarchical porosity, rational design, catalysis.**
Résumé	**Révéler l'importance de la structure cristalline des zéolithes**
	La conception sur mesure et le contrôle des propriétés de systèmes chimiques simultanément sur différentes échelles, de la molécule au cristal, demeurent un défi majeur. Les zéolithes, aluminosilicates cristallisés microporeux, représentent la famille de catalyseurs hétérogènes la plus utilisée en pétrochimie (alkylation, craquage, isomérisation) et comme milieu de confinement de cations métalliques. La conception rationnelle ainsi que l'élaboration maîtrisée de ces polymères inorganiques cristallins à structure parfaitement définie sont au cœur d'une recherche intensive. Ces recherches portent sur l'adaptation de la formulation moléculaire, la hiérarchisation de la porosité, le contrôle de la taille et de l'assemblage des cristaux, l'objectif étant de contrôler et d'adapter les propriétés de ces catalyseurs (acidité, dopage par métal, taille de la particule) pour une application visée et, si possible, de prédire leur réactivité.
Mots-clés	**Zéolithe, morphologie, cristallisation, porosité hiérarchisée, conception rationnelle, catalyse.**

Zeolites are remarkable microporous crystalline inorganic solids with regular porous structures (*figure 1*). These aluminosilicate materials, formed by interconnected cavities and channels ranging between 3 and 20 Å, present tunable acid-base properties [1]. Their properties can further be tuned by the accommodation of metal particles or complexes inside their channels or cages, or by introduction of different cations by ion-exchange.

The well-defined structures of each zeolite determine their framework type and the topology of the internal pore structure. The pore topology seriously affects the catalytic selectivity for a driven product, given the size of both molecule and pore aperture. One of the most important features of zeolites is thus their shape selectivity [2]. This amazing characteristic was evidenced, for instance in industry, by the use of ZSM-5 and related medium-pore zeolites as catalysts for the MTG (methanol-to-gasoline) reaction or xylene isomerization. Likewise, larger pore sized zeolite Y (cracking, hydrocracking, etc.) became a reference catalyst in fluid catalytic cracking processes. Zeolites have also been used as catalysts in a large palette of reactions, ranging from the selective catalytic reduction of nitrogen oxides (DeNO$_x$) from exhaust gases to organic synthesis [3].

Besides catalysis, zeolites are often used as molecular sieves for separation in membrane science but also in
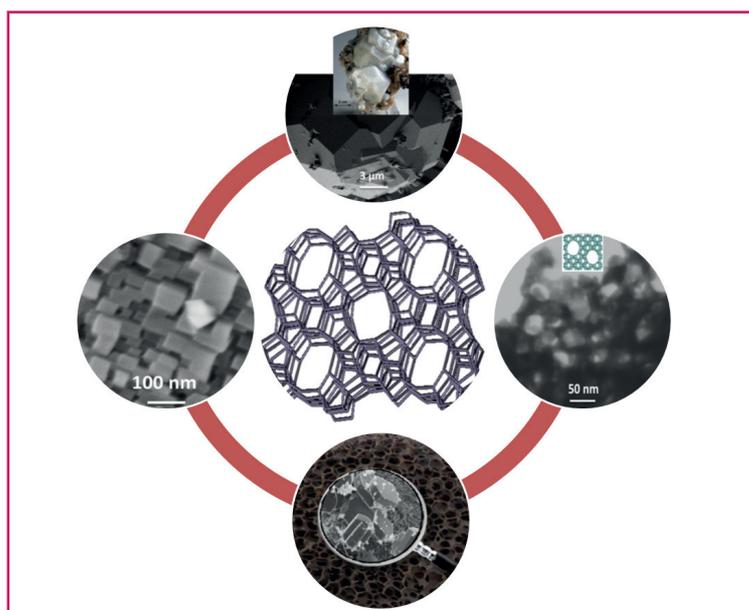

Figure 1 - Strategy to control the zeolite textural properties at the microscopic and macroscopic scales. Top: analcime natural and synthetic crystals; left: MFI zeolite nanocrystals exhibiting a rectangular French fries morphology; bottom: MFI crystals grown on SiC foam support; right: zeolite exhibiting large mesopores.

medicine and chemical sensing. Nevertheless, the main domain in catalysis which requires zeolites (around 90%) still remains oil refining and even petrochemistry in its globality [4]. Indeed, and although the unique aforementioned properties have opened the path to zeolite commercialization for industrial purposes, amongst the nearly 210 types of unique zeolite frameworks identified, only 20 types are actually applied in industry [5]. Among those, the community usually mentions the "big five" zeolites, being MFI, MOR, BEA, FAU and FER structures[1].

The quest for synthesizing new zeolites is now well-advanced but the following question arises: *is it worthy to move toward new discoveries or rather concentrate the efforts to improve the design of those "big five" structures?*

New zeolite synthesis

The development of new heterogeneous catalysts is a field with a tremendous impact in upgrading the efficiency of existing processes and in turning them more environmental friendly. Indeed, the replacement of homogeneous catalysts by heterogeneous ones has an increasing potential in environmental catalysis and in the synthesis of fine chemicals.

Although zeolites have found widespread catalytic applications mostly in petrochemistry, the sole presence of micropores imposes diffusion limitations that may hinder the rate of chemical reactions. The microporous network inside the zeolite represents both the main advantage (shape selectivity) and a major drawback (diffusional limitations) of these solids. Hence, the morphology and the size of the crystals have an important influence on the global reaction rate control, with impact on the *mass transfer* versus *reaction rate* game.

One strategy to overcome this problem is the synthesis of nano-sized crystals [6], where the diffusional path of molecules becomes shorter. However, the separation of nano-sized catalysts from a reaction mixture can be difficult due to the nature of the colloidal mixtures formed. Another approach consists of developing zeolites with larger pores. One may for instance cite the germanosilicate zeolite ITQ-37 with channel diameters up to roughly 20 Å [7]. The main challenge is to maintain the catalyst's shape selectivity, high surface area and acid-base properties (related to the Si/Al ratio) and eventually mesoporosity (pores comprised between 20 and 500 Å). The presence of mesoporosity can be observed in *figure 1* (right image).

The tuning of zeolite crystal shape and size can also be achieved by performing minor modifications of the synthesis conditions. The nature of silica source, hydrogel ageing conditions and composition, or eventual structure-directing agent (SDA) use, can greatly affect the zeolite crystallization outcome. These modifications can seriously affect the nature of the zeolite structure (and type) obtained and thus lead to an infinite combination of characteristics and properties, opening the door to a vast research field.

Pushing the boundaries of zeolite science

Hierarchical zeolites

Hierarchical zeolites combine at least two levels of porosity, in general *microporosity* (pore diameter < 20 Å) and *mesoporosity* (pore diameter between 20 and 500 Å). *Figure 2* shows the pore size distributions of a pristine faujasite-type
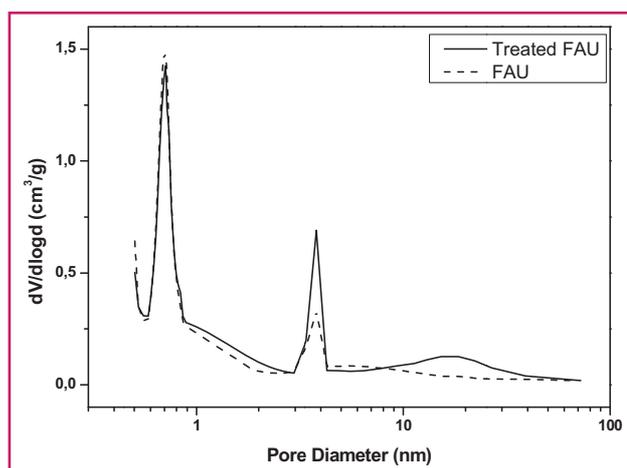

Figure 2 - Pore size distributions of pristine (dashed line) and chemically treated (solid line) FAU zeolites.

zeolite containing mainly micropores and the same zeolite after harsh chemical treatment. In the latter case, the raise in the mesopore region, *i.e.* 3-4 nm in size can be observed.

Several strategies have been proposed to synthesize those zeolites by performing the removal of framework atoms after zeolite synthesis, either dealumination [8] or desilication [9]. However, these *destructive methods* involve a loss of zeolite material and also the presence of irreversible damages within the zeolite structure. Another strategy is based on the use of surfactants as a second template to introduce mesoporosity. This *constructive method* is inspired by the syntheses of structured hexagonal mesoporous silicas MCM-41 [10] and SBA-15 [11]. Indeed, the formation of mesopores in these solids arises from surfactant use (as second template) to produce micelles with peculiar geometry, building thus the mesoporous network.

Another interesting technique to introduce mesoporosity in zeolites is the use of a second "hard-template". A sacrificial solid template is introduced in the zeolite synthesis gel, allowing the growth of the zeolite crystal around its structure. After completing the hydrothermal process, the template can be removed by combustion (in the case of organics) or dissolution (inorganic templates). The majority of such sacrificial templates building mesopores are organic molecules encapsulated within the zeolite crystals during their growth. This technique has led to numerous ingenious syntheses using imaginative templates, *i.e.* carbon nanotubes, pyrolyzed sucrose, surfactants, polymers, organic aerogels, and biological templates such as plants or bacteria. In spite proper control of the size of these holes having few billionths of a meter, carbon nanotubes are rather costly to be simply burned after the synthesis. However, one can perfectly tune the size of mesoporous holes and even replicate the sacrificial template by a clever choice of its size and morphology.

Control of the crystal morphology

The control of crystallization processes, based on the mastering of the chemical and physical conditions during zeolite synthesis, led to new specifically tailored catalysts for defined applications [12-13]. As aforementioned, one smart approach to tune the zeolite morphology is by the use of external additives. The necessary characteristics for this external agent are its availability, cost, non-toxicity and ease in manipulation. Bearing this in mind, we have recently added
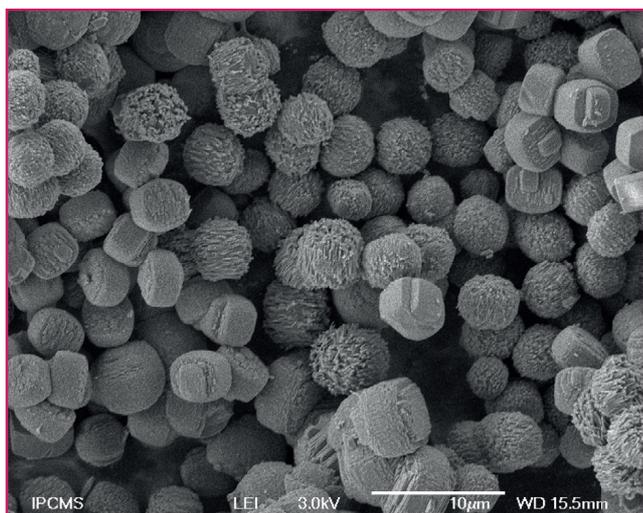
Figure 3 - SEM micrograph of a double crystallization mode of a ZSM-5 zeolite by addition of xylose.
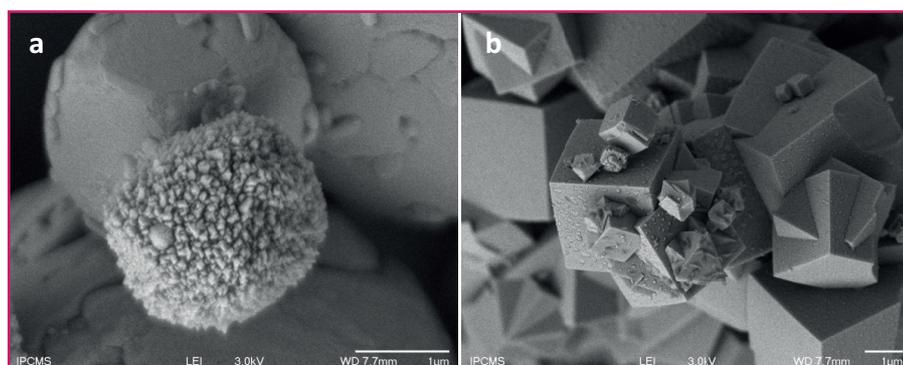

Figure 4 - SEM image of LTA zeolite crystals obtained a) after sugar cane bagasse residues addition to the gel; b) by extra-addition of sugars extracted from biomass.

monosaccharide molecules such as xylose and glucose to the zeolite synthesis mixture. The scanning electron microscopy (SEM) image (*figure 3*) shows the size and morphology of the crystals and evidenced a non-conventional double crystallization mode, upon introduction of xylose.

Likewise, we have also investigated the influence of biomass residues (containing various sugars) on the ZSM-5 zeolite crystals formation [14]. Crystals exhibiting a nano French fries-like morphology and a size comprised between 50 and 100 nm were formed after a proper tailoring of the gel composition (*figure 1*, left image). The latter zeolite allowed enhanced diffusional properties in comparison with micron-sized zeolite, thus leading to a higher selectivity toward light olefins formed in the cracking of n-hexane [14]. The novelty consisted of manufacturing hierarchical porous zeolite microspheres (diameter about 1 μm) formed by the self-aggregation of rectangular submicron units.

Keeping in mind the influence of saccharide addition on zeolite crystal morphology, we have found it worthwhile to synthesize various zeolite structures by adding sugar cane residues to the gel. Indeed, bagasse is the residue from valorization of sugar cane to produce either bioethanol or sugar. Besides other effects, bagasse behaves as a sacrificial template in the synthesis of several zeolites. *Figure 4* shows different crystal shapes observed for LTA-type zeolite after biomass addition. This LTA zeolite exhibits a rather rough surface indicating a higher specific area, being thus interesting for applications as molecular sieve for gas separation or in membranes technology [15].

Figure 4a shows zeolite crystals obtained by adding sugar cane bagasse to the zeolite synthesis. LTA-type zeolite crystals having a typical cubic shape and smooth facets are formed during conventional synthesis [16]. Likewise to the MFI zeolite formation, a double-mode of crystal growth could be evidenced for NaA zeolite when biomass residues were added to the mixture. Crystals having a cubic shape but less smooth and relatively rounder than pristine LTA-zeolite were formed. Besides, an aggregation of nanometric sub-units into a *litchi-like* superstructure can be observed (*figure 4a*). As for the MFI zeolite synthesis, a special self-organization occurred between the organic template and polymeric alumino-silica species *via* van der Waals interactions which governs the stability, the shape and the symmetry of the zeolite framework [17].

Supramolecular chemistry, developed by Jean-Marie Lehn, is obviously involved in the synthesis of zeolites, dealing with the formation and dynamics of molecular assemblies, resulting from the self-organization of several chemical species held together by intermolecular forces, *i.e.* non-covalent bonds [18].

To determine whether the biomass fibrous structure or its chemical composition were responsible for such crystal morphologies, we have added the alkaline hydrolysis solution of the vegetal to the LTA-zeolite synthesis mixture. *Figure 4b* represents a different LTA zeolite crystal morphology. In the later procedure, well defined cubes, having 0.5-3 μm in size, have been produced. A deeper focus on the surface evidenced both a high degree of crystal intergrowth and a high roughness present on the cube facets, thus indicating another crystal growth mechanism. By adapting the synthesis conditions, *i.e.* addition of sugars or biomass hard template, one may therefore be able to *tailor the crystal surface roughness, their morphology, size, assembly and hence their properties in various application fields*.

Zeolitization of solid supports

Owing to the small size of zeolite crystals (nanometric up to micrometric), the use of zeolites in industrial processes usually requires shaping the original particles into spheres or extruded pellets. More effectively, the binderless coating of zeolites over solid-supports can avoid many drawbacks encountered in industrial applications such as (a) high-pressure drop, (b) limited heat and mass transport rates, (c) axial dispersion leading to loss of selectivity, and (d) susceptibility to fouling by dust. Indeed, to overcome these problems, great efforts have been devoted in past decades to develop and optimize zeolite coatings onto structured supports constituted of stainless steel [19], ceramics, porous glass [20] or carbon. The support has to be carefully chosen to suit the required operating conditions. Firstly, the material should be chemically inert to avoid interference with the catalytic or chemical/physical process. Among ceramics, silicon carbide (SiC) is a rare material which associates the chemical inertness to several interesting properties, namely high thermal conductivity, mechanical resistance, excellent resistance to oxidation and ease of shaping [21]. Thus, it has found widespread applications in biotechnology, optics and electronics, sensing, membranes or as catalyst support.

In silicon carbide, each Si atom is bonded to four carbon atoms and *vice versa*, thus forming a tetrahedral diamond-like structure. Thanks to these light elements, SiC exhibits low thermal expansion coefficient and high thermal conductivity among ceramics. In addition, SiC is the third hardest compound known, right after diamond and boron carbide. Due to a certain ease in shaping, SiC is nowadays commercially available in different shapes, ranging from spheres to extrudates, rings, foams, etc. Silicon carbide can also crystallize into different structures, giving rise to a large number of polymorphs, distinguished by different stacking sequences in identical planes of Si and C atoms [21]. Amongst all polymorphs, β- and α-SiC are the most commonly used, due to their rather high specific area (β) and thermal conductivity (α), respectively. Using the expertise gathered in our group on the growth of zeolite crystals over glass [22], metal grids [19] or even β-SiC [23], the growth of MFI type zeolites was attempted over highly robust and thermally stable α-SiC foam support [24]. Due to the aluminosilicate nature of the zeolite crystals, their growth over α-SiC foams was performed in the presence of an aluminum precursor (sodium aluminate). Regarding the silicon precursor, the synthesis was either performed using tetraethylorthosilicate (TEOS) or without any external addition of silica source, thus using the silicon itself contained in the SiC structure. In the former case, the addition of TEOS resulted in the formation of MFI/SiC composites. In contrast, analcime zeolite crystals (ANA phase) were surprisingly grown on α-SiC *via* a self-recrystallization procedure [24]. Indeed, in this Al-rich gel, sodium ions (from sodium aluminate precursor) could play the template role and one may expect the formation of high Al-content zeolite.

Figure 5 clearly demonstrates the formation of well-dispersed analcime crystals onto α-SiC surface. The silicon carbide foam acts both as silicon source and as a support enhancing heat and mass transfers in catalysis. *Figure 1* presents a comparison between natural ANA crystals (10 cm in size) and a synthetic one. It is noteworthy that the later one is 10.000 times smaller than the crystal found in geological museum. This highlights the usual tendency to observe the formation of larger crystals in nature than in the laboratory. The synthesis conditions, the eventual presence of organic templates or the nature of Si and Al precursors, can therefore lead either to different zeolite structures or affect the crystal size and morphology. The innumerous paths in zeolite synthesis offer a wide range of possibilities for ingenious zeolite/SiC composites that can be tailored for defined applications.

Conclusions and perspectives

In conclusion, hierarchical zeolites have been synthesized in our group by the addition of hard-templates or by re-crystallization of solid supports. Compared to conventional zeolites, the introduction of mesoporosity by addition of a hard-template (from biomass residues) led to higher specific areas that induce better transport properties and hopefully improved catalytic or separation properties. Upon exploring the synthetic conditions, double crystallization modes have been observed for LTA and MFI-type zeolites, which may induce peculiar catalytic properties of these crystals. One may for instance imagine the possibility to achieve different selectivities for one single zeolite catalyst arising from these different crystal morphologies. The coating of ZSM-5 and ANA zeolites over α-SiC have also been demonstrated, aiming at the improvement of the thermal properties of the zeolite.

Figure 5 - SEM images of analcime (ANA) crystals coated on SiC support by self-recrystallization.

The examples provided in this article highlight the numerous possibilities offered by tuning the synthesis conditions, leading to newly shaped zeolites or zeolite composites (*figure 1*). Although the topology and crystalline structure of these solids is now well-understood, the mechanistic pathways in zeolite formation still catch a lot of scientific attention. Some recent articles shed some light in understanding a few zeolite structures formation [25], however the *full-screen* mechanism remains a *chimaera*. An ambitious goal would then be a thorough study of the influence of external additives on the formation of hierarchical zeolites, helping thus the prediction of the crystal morphology. The zeolites and zeolite composites synthesized by this way would possess controlled size and shape and thus, tailored properties for specific applications.

Note and references

(1) The *Atlas of Zeolite Framework Types* [16] published by the International Zeolite Association assigns a three letter code defining each known framework topology. This designation usually derives from the name of the zeolite or "type material", e.g. FAU for molecular sieves with a faujasite topology, e.g. MFI for the ZSM-5 (Zeolite Socony Mobil) and silicalite topologies.
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vient de paraître

Chimie et expertise
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