Review Article

Ordered Porous Nanomaterials: The Merit of Small

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This paper will introduce the reader to some of the "classical" and "new" families of ordered porous materials which have arisen throughout the past decades and/or years. From what is perhaps the best-known family of zeolites, which even now to this day is under constant research, to the exciting new family of hierarchical porous materials, the number of strategies, structures, porous textures, and potential applications grows with every passing day. We will attempt to put these new families into perspective from a synthetic and applied point of view in order to give the reader as broad a perspective as possible into these exciting materials.

"This work is dedicated to Professor Vicente Berenguer-Navarro"

1. Introduction

Considering the history of mankind, its development is unavoidably linked to technology, more precisely to the development of materials and methods which have enabled us to go beyond our own frontiers. Focusing more on the matter at hand, which is porous materials, we can find several remarkable examples throughout ancient and modern history about the use of porous carbon materials for a wide variety of applications. For instance, in 3700 BC we find the earliest use of a porous form of carbon. Charcoal was used by Egyptians and Sumerians for the reduction of different metal ores (mainly copper, tin, and zinc) in the manufacture of bronze. This material was also used as domestic smokeless fuel. This example alone clearly shows how even some of the most advanced civilizations of their time have employed porous materials in their technological tree. The earliest recorded example in which porosity of the material comes fully into play is in 1500 BC, in Egyptian papyri describing the use of charcoal to adsorb odorous vapors from infected wounds and from within the intestinal tract. The fact that we find these very early examples linked to a civilization which dominated a vast empire for several thousands of years should come as no coincidence. In 450 BC we can find

excellent examples of how the porosity of carbon materials is employed as a means to purify drinking water in Hindu documentation and in Phoenician trading ship records. In 400 BC Hippocrates and Pliny the Elder recorded the use of charcoal to treat a wide range of illnesses and maladies including epilepsy, chlorosis, and anthrax. In short, porous materials have greatly helped modern civilizations from the very infancy of mankind, and even if in ancient times the people could only guess as to how or why they worked, the fact is that their usefulness is very well documented. Presently, carbon materials are undoubtedly crucial in many areas of technological development, with applications ranging from household use in water purification systems or as odour filters [1] to adsorption compressors as cooling system in space telescopes [2], but these materials are composed of the irregular stacking of graphene sheets which give rise to slit-shaped pores [3]. As the philosopher Blaise Pascal expressed in the 17th century, "Man is but a reed, the most feeble thing in nature; but he is a thinking reed." Thus, the underlying and undeniable merit of science is that we now possess the tools not only to know the reason why porous materials are so useful, but also to be able to control their porous texture to make materials with on-demand porosity and properties.

This starting paragraph should be taken merely as an illustrative standpoint which shows the importance of porous materials. During this paper we will attempt to analyse in detail some of the most prominent classes of ordered porous materials from both a synthetic and applied point of view. Thus, classical carbon materials as those described in the previous paragraph fall outside the scope of this paper. In this respect, it must be mentioned that the term "ordered" does not necessarily mean that the prepared materials should possess high structural order, but in fact the term applies to the porosity of the material itself. Throughout the paper we will come across several examples of materials which, despite possessing walls formed by amorphous solids possess a regular (i.e., ordered) porous array which, in turn, results in clear indications of a crystalline or, at least, of a crystal-like structure. Perhaps one of the earliest and best-known examples is that of the material known as MCM-41 [4, 5], which despite being composed of amorphous silica, presents a distinctive X-Ray Diffraction (XRD) pattern due to the hexagonal array of mesopores it possesses.

Since this paper encompasses a broad array of porous materials, we will not go into excessive detail on any of the topics described henceforth. Should more information on one specific class or type of materials be required, the reader is strongly encouraged to go through some of the references which will be presented here for more detailed information.

2. Zeolites

2.1. History. The term *zeolite* was first used in 1756 when Cronstedt, a Swedish geologist, published a research paper in which he described a mineral which released water upon heating, but could recover it reversibly at low temperatures [6]. The term derives from the greek words *zein* (to boil) and *lithos* (stone). The mineral in particular which Cronstedt described is nowadays known as stilbite and belongs to a large family of crystalline solids both natural and man-made, known as zeolites.

Some important milestones in the history of zeolites are shown in Table 1.

In short, the history of man-made zeolites can be traced back to the laboratory preparation of levynite by de St. Claire-Deville in 1862. Nevertheless, zeolite synthesis as it is known and commonly carried nowadays had its origins in the research of Barrer and Milton, commencing in the late 1940s. Barrer began his work by investigating the conversion of mineral phases in the presence of strong salt solutions at moderate-to-high temperatures (between 170 and 270°C) [18–20]. One of the obtained products in these experiments resulted in the first synthetic zeolite (i.e., the first zeolite unknown as a natural mineral). On the other hand, Milton pioneered the use of more reactive starting materials, such as aluminosilicate gels of recent preparation, allowing for reactions to be completed under milder experimental conditions, which ultimately lead to the discovery of different zeolite structures [21, 22]. By 1953, Milton and his coworkers had synthesized 20 zeolites, including 14 unknown as natural minerals [23].

TABLE 1

1858	Eichorn points out the ion-exchange capability of zeolites [7]
1862	de St. Claire-Deville synthesizes the first artificial zeolite, levynite [8]
1876–1905	Studies on ion-exchange in zeolites [9–11]
1930	Taylor reveals the structure of analcime [12]
1932	McBain introduces the term *molecular sieve* [13]
1938	Barrer presents a remarkable work on molecular sieving [14]
1940–1945	Reports on zeolite molecular sieves with different pore sizes
1950–1972	Synthesis of Zeolites A [15], X, and Y [16], and ZSM-5 [17]

In 1960, Flanigen and Breck studied in detail the formation mechanism of zeolites. They reported the use of X-Ray measurements to follow the crystallization of different zeolites over time [24, 25]. They were the first to observe the S-shaped growth curves typical for zeolite synthesis, which indicates the induction period during which few zeolite crystals are formed, followed by a rapid growth which takes place over a short span of time. The observed morphological changes were described as a successive ordering of the gel as crystallization takes place [26, 27]. This led the authors to the conclusion that crystal formation is mainly a phenomenon that takes place in the solid phase.

2.2. Synthesis and Structure. The interest raised in zeolites throughout the scientific community has been growing ever since the aforementioned pioneering works up to the point that research related to both synthesis and application of these materials and some of their related families has been growing for the past decades. Perhaps the best example to illustrate this point is the fact that the number of synthetic zeolites has widely surpassed that of natural ones.

A zeolite is a crystalline aluminosilicate with a structure based in an open three-dimensional network which presents pores or channels [28, 29], which in turn confers them very interesting properties [30]. Bearing in mind the definition of "zeolite" implies that all compounds with a similar (or even the same) structure but made up of other materials, such as silicates, or metaloaluminates, are known as zeotypes [31]. In this respect, Al^{3+} ions have been substituted by other ions such as B^{3+}, Ga^{3+}, Fe^{3+}, and Cr^{3+}, and Si^{4+} has been substituted by Ge^{4+} or Ti^{4+}. In this respect, and as a reflection of the great technological importance and complexity that zeolites involve nowadays, compounds such as aluminophosphates ($AlPO_4$), silicoaluminophosphates (SAPO), and other similar compounds.

The structure and composition of zeolites depends on the zeolite type in question [32]. Zeolites are formed by oxide anions (O^{2-}) forming tetrahedral structures. The Si^{4+} and Al^{3+} ions are located in the center of the said tetrahedra.

TABLE 2: Types of zeolites attending to their pore size.

Zeolite type	Number of TO_4 forming the pore	Pore diameter (nm)	Examples
Extra-large pore	≥ 14	$\phi > 0.9$	$AlPO_4$-8, VPI-5
Large pore	12	$0.6 < \phi < 0.9$	Y, Mordenite, β, Ω
Medium pore	10	$0.5 < \phi < 0.6$	ZSM-5, ZSM-11
Small pore	8	$0.3 < \phi < 0.5$	Erionite, A, SAPO-34

The proportion between silicon and aluminium ions (the so-called Si/Al ratio) determines the framework charge. In order to compensate the negative charge derived from the presence of the aluminium atoms, different cations are incorporated in extra-framework positions, which grants zeolites one of their most interesting, which is the ion-exchange capability.

Thus, the empirical formula for a zeolite would be as follows:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O, \qquad (1)$$
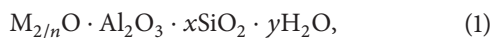
where "M" represents the interchangeable ion and "n" reflects its oxidation state. Löewenstein's rule [33] points out that two $[AlO_4]^{5-}$ units cannot be in adjacent positions, which means that "x" will always be higher than or equal to 2.

Perhaps one of the most intuitive description of a zeolitic structure is based on its pore size; thus, zeolites may be classified according to the number of tetrahedral, (TO_4, being "T" either Si or Al) which define the pore aperture size. Table 2 shows this classification.

As it is well known nowadays, zeolites are prepared by means of hydrothermal synthesis [34] of the suitable precursor silicoaluminate species in a sealed reaction vessel, usually a teflon-lined autoclave. A typical hydrothermal zeolite synthesis may be described in the following terms.

(i) Amorphous precursors containing silica and alumina are dissolved together with a cation source, usually in a basic medium. In this respect, it is common to use alkali ion hydroxides (also known as mineralizing agents) to reach the necessary high pH values;

(ii) the aqueous reaction mixture is heated, often in a sealed reactor. In other cases, the reactor is directly inserted in a preheated oven;

(iii) the reactants remain amorphous for some time, even after reaching the onset temperature;

(iv) after the aforementioned "induction period," formation of the first zeolites crystals is observed;

(v) all amorphous material present in the solution transforms into an approximately equal mass of zeolite crystals. These may be recovered by filtration, washing, and drying.

In a typical representative synthesis, a zeolite may be synthesized from sodium metasilicate (water glass) and sodium aluminate under hydrothermal conditions. Once the aluminate is added on the silicate a gel is formed in which aluminate and silicate oligomer chains and cycles coexist, with different degrees of ramification. This is known as precrystalline phase. The chemical composition (silicon/aluminium ratio, pH, nature and purity of the reagents, and order of addition) will play a key role in the characteristics of this first phase. When we start to heat up the mixture, these chains and cycles depolymerize, giving rise to smaller units. This first process produces free TO_4 units, which constitute the Primary Building Units (PBUs). These tetrahedra will rearrange under hydrothermal conditions giving rise to the Secondary Building Units (SBUs). It must be noted that during this condensation process, all the oxygen ions located at the apexes of each tetrahedron are shared by two tetrahedra. At this stage of the synthesis, the SBUs will start to arrange themselves around a certain chemical species called "template" or "SDA" (Structure Directing Agent) which is added into the reaction solution. This template is of critical importance, as the reader will notice throughout this paper, since depending on which molecule is used as template, the SBUs will arrange in one fashion or another, giving rise to the Tertiary or Composite Building Units (TBUs, Figure 1). Further condensation of these species will form the polyhedra, which upon assembly under the right conditions will result in the final zeolite product (Figure 2).

During hydrothermal synthesis and in the presence of the aforementioned mineralising agent, the crystalline zeolite product, which contains Si–O–Al bonds, is created. Since the bond type of the zeolite is very similar to that of the precursor oxides (namely, Si–O and Al–O bonds), no significant enthalpy change is involved in the process (Figure 3). Actually, the overall free energy change for a zeolite synthesis reaction is usually quite small. Thus, the result of a zeolite synthesis is predominantly controlled by the kinetics of the whole process [35–39].

Kinetic control is the main driving force during zeolite synthesis, especially taking into account that zeolites are metastable phases in most cases. Much of the current knowledge in these industrially important materials involves precise control over the synthesis conditions aimed at product optimisation, so that the materials can be prepared on-demand with a high degree of reproducibility [34].

One rather surprising feature involving zeolite crystallization is that the exact synthesis mechanism is still under intense scrutiny. From the first proposed mechanism by Barrer and coworkers [41], several other authors have attempted to explain the transformation of amorphous silicon and aluminium species into crystalline zeolites. In [41] we find this possible explanation for this mechanism:

> "The formation of diverse kinds of structural framework leads to questions as to the mechanism of growth. The phases are often obtained reproducibly in yields nearing 100% and the free-energy balance between the many possible aluminosilicate nuclei must be delicate. The development of elaborate and continued space patterns by progressive additions of single $(Al,Si)O_4$ tetrahedra is difficult to imagine, particularly in the case
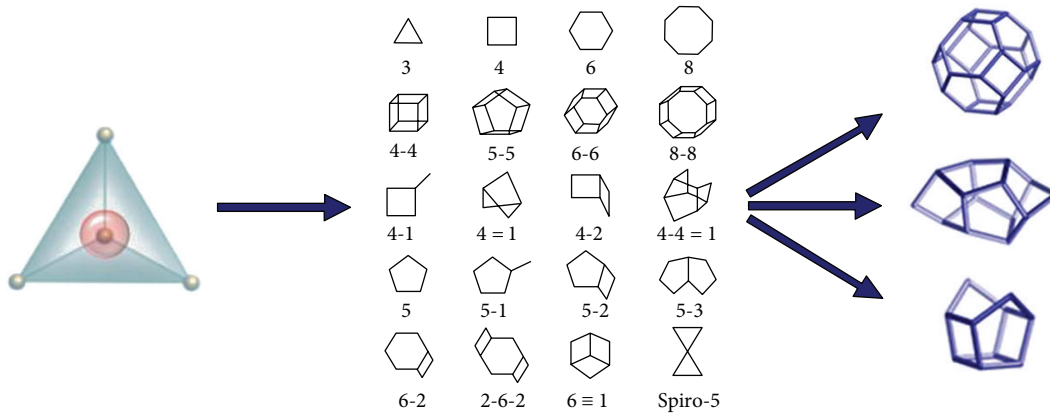
FIGURE 1: Left to right, schematic representation of a PBU (oxygen ions represented by the small spheres, the T ion represented by the larger sphere), examples of SBUs (taken from [35]), and examples of TBUs formed form the SBUs. Note that in the representation of both the SBUs and TBUs the "T" ions sit at the vertices while the O ions are located in the middle of the aristae. This is done for the sake of simplicity.
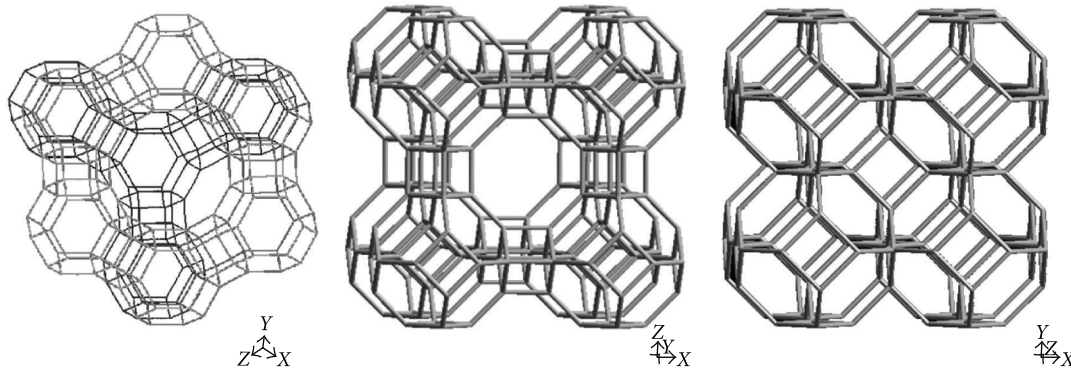

FIGURE 2: Scheme of some zeolites derived from the TBUs. Left to right: Faujasite (FAU, zeolite X and Y), Zeolite A (LTA), and Sodalite (SOD).
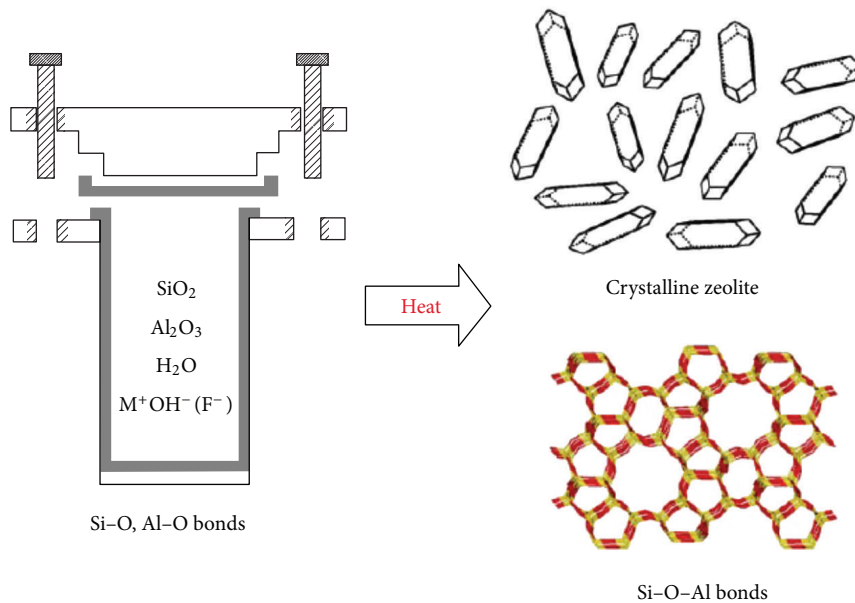

FIGURE 3: Schematics of hydrothermal zeolite synthesis. The starting materials are converted into the crystalline products under the effect of the temperature, autogenous pressure, and the presence of an aqueous mineralizing agent (OH^- and/or F^- ions). Scheme taken from [40].

of very open zeolite structures. The formation of these frameworks is, however, much more easily visualised if in the aqueous crystallising magma there are secondary building units in the form of rings of tetrahedra or polyhedra. These may pack in various simple coordinations to yield different aluminosilicates."

During the 1960s, Flanigen and Breck conducted a series of pioneering studies which led to the following conclusions concerning the zeolite crystallisation mechanism.

(1) Nucleation takes place in a heterogeneous way during the formation of highly supersaturated gels within the synthesis solution;

(2) the crystalline nuclei do not necessarily represent a unit cell but may consist of more primitive preliminary building units as those suggested by Barrer et al. [41];

(3) during the induction period (i.e., the time during which very little zeolite is formed), the nuclei grow in order to reach a critical size which will prevent their dissolution and then grow rapidly to form small and uniform sized crystals;

(4) growth of the crystalline species proceeds through a type of construction and deconstruction process (cleaving and reforming Si, Al–O–Si, Al bonds), catalyzed by excess hydroxyl ion and involving both the solid and liquid phases (although the solid phase appears to play the predominant role).

In 1966 Kerr reported an experiment [42] in order to test the following reported hypothesis: "a zeolite could be formed via dissolution of gel by sodium hydroxide solvent followed by deposition of zeolite crystals from gel-derived species in solution." [43]. From his observations, Kerr concluded that the involved the rapid dissolution of the amorphous phase in the synthesis solution to yield soluble species. The rate-limiting step was the incorporation of these latter species into stable crystalline nuclei which resulted in the final zeolite product. Later in the same decade, Ciric [44] presented a very detailed study on the growth of zeolite crystals. His observations included a wide variety of techniques such as microscopy, adsorption measurements, and chemical analyses, and pointed towards a growth mechanism in which solution mediated the process with the participation of a gel phase present. In this respect, Ciric pointed out that his conclusions were consistent with those of Barrer and Flanigen-Breck.

At the turn of the 1970s, Zhdanov presented a very important contribution to the 2nd International Zeolite Conference [45] in which he presented his results on the measurements of crystal growth rates. He clearly showed the influence of temperature on the zeolite growth rate, which led him to deduce the nucleation rate profile during reaction, thus providing the scientific community with a chemical perspective into the phenomenon of zeolite crystallisation. In this view, the solid and liquid phases are connected by the equilibrium in solution. Condensation reactions give rise to "primary aluminosilicate block" and crystal nuclei. Crystal growth occurs from solution until dissolution of the amorphous phase is complete under the effect of the mineralizing agent (OH^- or F^- ions). From those studies, the role of the solution phase in the zeolite formation mechanism became increasingly important, as evidenced by several different experiments. In this respect, Angell and Flank [46] reached some conclusions different from those reported by McNicol and coworkers [47, 48] after using Raman spectroscopy, XRD, and particle size analyses. The former study was later supported by the reports by Culfaz and Sand [49] and Kacirek and Lechert [50] which concluded that the rate-determining step was the linking of silicate species to the surface of the crystal. They also pointed out that, under their conditions, the solution phase would contain essentially only monomers and dimers during the crystallisation zeolites with high aluminium contents, with larger oligomers (perhaps up to Si_{20}) present in the synthesis of the more silica-rich zeolites.

From the 1980s onward, the most relevant studies on zeolite growth focused on the study of zeolites of the MFI type, namely, zeolite ZSM-5 with different Si/Al ratios [51, 52]. The group of Derouane and Blom described in a series of papers that according to their observations, there appeared to be two different [53–57] mechanisms for the formation of ZSM-5 zeolite. When a low Si/Al ratio was pursued and polymeric silica species were employed, the mechanism involved the transportation of ions in the liquid phase to yield large zeolite crystals. On the other hand, in the case of high Si/Al ratios and when using monomeric silica species such as water glass, their observations suggest the formation of several nuclei which gave rise to a large number of small ZSM-5 crystallites directly within the hydrogel in a process described as a solid hydrogel phase transformation. The experiments performed by Chang and Bell [58] pointed at the formation of template-silicate clathrates which were as "embryos" by ordering themselves into zeolite nuclei under the effect of the mineralising agent, which would be responsive for the cleavage and recombination of Si–O–Al bonds. Burkett and Davis [59–61] took this idea further by investigating the role of different structure directing agents in the synthesis of silicalite (the all-silica zeotype for the MFI framework) by MAS-NMR spectroscopy. Their conclusions indicated that zeolite crystallisation occurs via the formation of organic-inorganic composites which are organised in the synthesis solution to form the first crystal nuclei through aggregation. Further incorporation of these composites to the nuclei gives rise to a layer-by-layer growth of the final zeolite product, as shown in Figure 4.

One of the most recent and detailed studies on the crystallization mechanism of zeolites is owed to the group of Martens and Jacobs at the Catholic University of Leuven [62–66], where they described the zeolite formation originating from "nanoslabs" with very small dimensions which contained one SDA molecule each. More recent studies [67, 68] pointed towards a type of silicate oligomer as the primary constituent for the nanoslabs.

From this brief review, it becomes obvious that the formation of zeolites is a complex process which involves not only
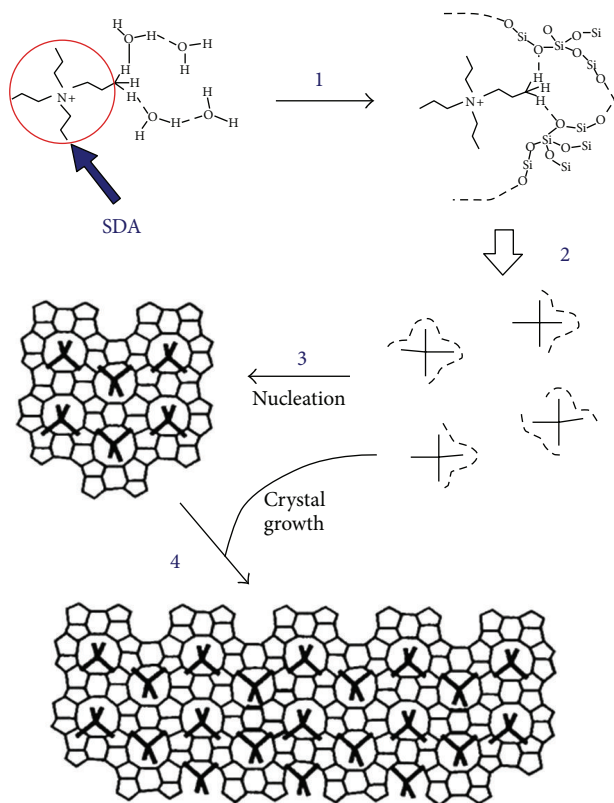
FIGURE 4: Scheme for zeolite crystallization adapted from [59]. The process is divided into the following stages: (1) formation of hydrogen bonds between the structure directing agent (SDA) and the silicates present in the synthesis solution; (2) oligomerisation of silicates; (3) condensation of the silicate-SDA species to give the first stable crystalline nuclei; (4) crystal growth. Note the tetrapropylammonium ions circled in red which act as SDA in this case.

many chemical species under the hydrothermal synthesis conditions, but also a significant number of processes that are involved in the crystallization processes. More recent studies have highlighted the key importance of the mineralizing agent, whose primary task is to convert the reactants into mobile and reactive forms, thus enabling the synthesis to move forward. For a more detailed review on the synthesis of zeolites and the study of the crystallization mechanism, an excellent review by Cundy and Cox covers this aspect in great detail [40].

Let us now turn our attention to a concept which is of the highest importance from a synthetic point of view, and which is ultimately the cornerstone of this review. The Oxford English Dictionary defines the term *template* as "an instrument used as a gauge or guide in bringing any piece of work to the desired shape." In the case of zeolites, as mentioned above, the initial silicoaluminate oligomers cluster around the template to give rise to the final zeolite structure. The first reports on the preparation of synthetic zeolites described the hydrothermal treatment of silicoaluminate gels in an aqueous solution in the presence of a mineralising agent [18, 19]. In 1961, two different research groups explained

the effect of introducing quaternary ammonium cations in the synthesis of zeolites. This gave rise to the first amine-templated synthesis of zeolites A and X [69] and ZK-4 [70, 71]. One of the early pioneering studies on zeolite crystallization in the presence of mixed alkali-organic bases described the observed structure specificity with the different cations present in the synthesis solution, thus coining the term "templating" of the different cage structures by the larger organic and smaller alkali cations [72]. In a following study of the role of different cations, Khatami postulated that in the synthesis of zeolites from solutions containing cations with different ramifications, "the zeolite framework structure is determined by one or at most two cations depending on their type and size. Additional cations, should they be included in the lattice, affect the zeolite properties but have minimal or no influence on the structure topology." [73]. In 1983 Lok and coworkers published an extensive review on the role of organic molecules in molecular sieve synthesis [74], focusing on the charge distribution and the size and geometric shape of the template in order to explain the zeolite structure development. By that time it was already known that (1) a single template can form several different structures, (2) many templates can give rise to the same structure, and (3) some structures are template-specific. The solution to this problem was the relationship between templating and "gel chemistry" where "gel chemistry" represents all the reaction parameters governing the gel, such as oxide composition, temperature, time, reagent type, and pH. From a more practical perspective, the template became a necessary means but not a sufficient condition for structure development. With the passing of time, larger and more complex organic cations were employed as templates, resulting in structures which had the organic template filling not just cages, but channels (ZSM-48) [75] and channel intersections (ZSM-5) [52]. Further efforts in zeolite synthesis resulted in the use of nitrogen-free species as suitable templates for the development of zeolite structures, such as polyelectrolites [76], crown ethers [77], or metallocenes [78]. Zeolite science delves mainly in the understanding of shape selectivity and in the rational synthesis of new zeolite structures with tunable and desirable properties. In this sense, the use of computer simulation experiments can prove a great help, as pioneering studies have clearly shown the potential of studying the host/guest interactions (i.e., the interactions between template and the inorganic framework [79–81]). In summary, it is nowadays well known that different molecules can act as templates to give rise to a very wide variety of zeolite frameworks. According to the Structure Commission [82] of the International Zeolite Association [83], 201 zeolite framework codes are known, with the latest entry registered on October 15, 2011, which clearly show that even today zeolites attract great interest. The early works on zeolite synthesis used the hydrated alkali cations as templates (such as Na^+ ions in the synthesis of zeolite A or Na^+/K^+ ions in the synthesis of JBW zeolite [84–86]), and this evolved into the use of ternary and quaternary ammonium ions which has continued to our days. The effectiveness, variety, availability, stability, and cost of the nitrogen-based cations as templates are yet to be rivaled by any of the other aforementioned templates to date.

TABLE 3: Properties and applications of zeolites.

Property	Application
Ordered cannel structure	Adsorbent materials
	Molecular sieves
	Catalyst supports
	Selective catalysis
Ion exchange	Cation exchangers
	Dispersion of supported catalysts (ion exchange followed by reduction)
	Possibility of producing acid sites (ion exchange of NH_4^+ and desorption)
Acid sites present in the structure	Catalysis
	Adsorption of polar molecules

TABLE 4: Historic use of inorganic materials as detergent builders.

Year	Builder
1907	Silicate (water glass) + carbonate
1933	Diphosphate
1946	Triphosphate
1976	Zeolite A + triphosphate
1983	Zeolite A + carbonate + cobuilders[*]
1994	Zeolite A + special silicates[**] + cobuilders
1994	Zeolite P + carbonate (+cobuilders)
1997	Zeolite X + carbonate (+cobuilders)
1999–present	Zeolite AX (+carbonate + cobuilders)

[*] Polycarbonates or citrate, for instance.
[**] Amorphous or crystalline disilicates.

2.3. Applications. The applications of both natural and synthetic zeolites are a direct consequence of their specific features. Benefitting from their structure presenting a regular array of channels with molecular sizes, zeolites have been widely used as adsorbent materials and as molecular sieves. Furthermore, the excess negative framework charge which was mentioned above, as a consequence of the presence of tetracoordinated aluminium ions, is compensated by cations which may be easily exchanged, making zeolites excellent ion exchangers. Finally, the presence of framework acid sites, and the possibility of introducing new and tunable acid sites makes zeolites very active catalysts with very important applications, especially in pharmaceutical and petrochemical industry. We will elaborate all these points further, but Table 3 should serve as a summary of the main features of zeolites and some of the applications derived from them.

After having crossed the threshold of the new millennium, the attention of the detergent industry has focused on delivering clear and concise answers against four challenges [87]:

(i) economics,

(ii) safety and environment,

(iii) technology,

(iv) consumer requirements.

The crucial factor of the four is still the consumer. Although washing habits differ greatly from country to country, there is a trend towards easier handling (compact powders, tablets) of detergents with increased efficiency. First and foremost, however, the consumer continues to demand a clean wash combined with maximum protection of the items laundered. The resulting demand to continuously improve on the performance of detergents is leading to the use of new and/or optimized raw materials.

To a large degree, the aforementioned challenges dominated the development of detergents by the end of the 20th century. Zeolites, originally designed as a phosphate substitute for purely environmental reasons, had to meet the increasing demands imposed by modified detergent composition and production technologies. In particular, the trend towards compact detergents increased the demand for builder systems with a high adsorption capacity for liquid components, especially for surfactants. Zeolite A, introduced approximately 35 years ago, proved to be a good surfactants carrier and in the 90s advanced to become the builder leading to compact and supercompact detergents. Nevertheless, the demands from the market to bring on new improvements kept coming.

The manufacturers of detergent zeolites responded to the demand for higher standards of performance and processing by developing new zeolite grades. These include the zeolites of types P, X, and AX, which have all been introduced into the market during the past years. The main drawback of Zeolite A as zeolite builder was that it had a poor magnesium exchange capacity due to the hydrate shell surrounding the Mg^{2+} ions. Recently a new type of Zeolite P was developed with a high calcium exchange capacity. The new type, also referred to as zeolite MAP [88, 89], possesses a flexible, layered crystal structure. As a result of the slightly narrower pores (of approximately 0.3 nm) than Zeolite A, and the more flexible, adaptable crystal structure, the calcium ions are bound more firmly than in the case of Zeolite A.

Following the development of a more economically viable production process, Zeolite X was recently introduced into the market for detergents [90]. Like Zeolite P, the chemical composition of this zeolite is also virtually identical to that of Zeolite A. As with Zeolite A, the basic building blocks of Zeolite X are cubo-octahedrons, which are linked forming the zeolite structure via 6 membered rings (see Figure 2). Due to its larger pore diameter (0.74 nm), Zeolite X is capable of more readily incorporating magnesium ions. The result is a significantly higher magnesium binding capacity compared to Zeolite A and Zeolite P.

A further new development on the market is a cocrystallite comprised of 80% Zeolite X and 20% Zeolite A [91]. This grade, referred to as Zeolite AX, displays calcium and magnesium exchange properties which are superior to those of a blend of the pure zeolites (see Table 4).

We have covered the first one of the two major applications of zeolites in modern industry. The second field in which zeolites have by far the most outstanding impact from an economical perspective is of course the petrochemical industry [92]. In the 1960s, the application of catalytic properties of

zeolites for petrochemical processes was discovered. By the end of the 20th century, around 300,000 tons of synthetic zeolites were being used annually in catalytic and adsorptive applications. By 2008, the figure soared to almost 4 million tons (3.9), with an expected increase to over 4.1 million in 2011 [93, 94], with an expected business of over 17 billion dollars [93], making the petrochemical industry the largest market for synthetic zeolites by a large margin.

During the second half of the 20th century, the industrial application of zeolites and more general purpose molecular sieves emerged in full. The majority of the chemicals that constitute our consumers goods basis and energy carriers/vectors like transportation fuels have passed through the micro- and mesopores of these materials or materials derived from them. Some zeolite structures, mainly MFI and FAU and to a minor extend also MOR, are very versatile materials; that is, their properties can be tuned to the specific requirements of different applications, thanks mainly to the fine tuning of the Si/Al ratio and the ion exchange of the extra-framework cation. In a very detailed survey, Tanabe and Hölderich [95] described 124 acid-base catalyzed processes which had been commercialized or had been proposed for commercialization, of which 74 were zeolite-based, which once again points out the great relevance of these porous solids. In the specific case of petrochemical industry, the exceptional properties of zeolites make them highly attractive [96].

It must be considered that oil refining is in itself a very complex industry, involving many different processes. This is covered in some excellent reviews [97–100]. In a very short and concise way, a modern refinery has a three-fold function:

(i) adjust the crude oils supply in order to increase the H/C to make products which fit specific market needs;

(ii) remove pollutants present in feedstocks or during the refining processes (metals, N, S,...);

(iii) be efficient, both in terms of thermal efficiency and carbon/hydrocarbon efficiency. Typical carbon efficiency for a refinery is above 90%, which results in the best E-factor (ratio of mass unit byproduct per mass unit of desired product) for several industry segments [101].

Some of the processes in which we may find zeolites inside a refinery include the following.

(i) Light hydrocarbon (C_{5-6}) paraffins hydroisomerization [102–104]: the objective of this reaction is to branch different linear hydrocarbons in order to increase the octane numbers (both Research Octane Number (RON) and Motor Octane Number (MON)). This application is very interesting since the alternatives have major drawbacks concerning safety (H_2SO_4 or HF) or environmental regulations (FCC naphtha). In this respect, zeolite MOR (mordenite) has proven to be a more than apt acidic support for Pt catalysts [105].

(ii) Cracking and hydrocracking of heavy feedstocks: this includes Fluid Catalytic Cracking (FCC) and HydroCracking (HDC). The aim of these processes is to adjust the H/C ratio, either by rejecting a certain fraction of the feedstocks which is converted into coke on a monofunctional acidic catalyst (FCC), or by incorporating hydrogen with a bifunctional catalyst (i.e., acidic and metallic) (HDC). In the former case, zeolite Y from the FAU zeolite framework is extensively used in this application in different forms [106] such as ultrastabilized Y zeolite (USY), rare-earth exchanged USY (REUSY), rare-earth partially exchanged Y zeolite (REHY), fully rare-earth exchanged Y zeolite (REY). In the latter case, zeolite Y also plays a key role [107]. The zeolite Y used in HDC is dealuminated; it brings forth high activity (high acid site strength), stability (low coke make and resistance to nitrogen-containing poisons compared to pure amorphous silica-aluminas) together with a good accessibility due to the presence of mesopores generated during the steam dealumination process.

(iii) Aromatics production: despite the fact that the majority of aromatics is still obtained in the catalytic reformer of a refinery or recovered as byproduct in cracking of liquid hydrocarbons [108], several zeolite based-processes have been proposed in the past years. These processes make use of a MFI-type zeolite (ZSM-5) exchanged with different cations or mixed with different salts [109, 110]. These new processes upgrade low-value intermediate streams or refinery and steam cracker byproducts [111].

(iv) Aromatics processing: this includes disproportionation, intramolecular isomerization, aromatic alkylation, and hydrodealkylation. These processes have as main goal the production of benzene and xylene, and the different zeolites involved include ZSM-5 (MFI) loaded with platinum, mordenite (MOR), zeolite BETA (BEA*), and Ba or K-exchanged zeolite X (FAU) [112–114].

(v) Emerging technologies: a few examples include the hydrocracking of heavy aromatics into light paraffins [115], solid acid alkylation [116], skeletal isomerization of butene and pentene [117], or the methanol-to-olefins reaction [118]. The first two examples describe technologies which provide improvements over existing ones, while the other two use new feedstocks for end-products for which there already is a large demand.

In addition to these two very prominent applications, zeolites have found many other uses in our daily life. At the beginning of the 21st century, zeolites are applied in the development of new construction materials since they bring forth both an ion-exchange and an adsorption function, to solve problems in construction engineering according to different practical requirements [119], the removal of heavy metal ion from industrial waste water [120], or as food additives in order to modify or improve the quality of consumer goods [121]. The application of zeolites (both natural and synthetic) that show a greater social impact is that of environmental

remediation, which is a direct consequence of their ion-exchange and adsorption capacity. This includes the removal of heavy metals from soils and water streams [122, 123] or the ability to bind pathogens in order to remove them from wastewater treatment plants, thus including sludge activity [124, 125]. The outstanding relevance of zeolites is further illustrated by the number of reviews and research papers available in the literature covering topics as diverse as their use in catalysis (with reviews dating back to 1971 [126, 127]), pollution control [128], electrochemistry (zeolites may act as electrode modifiers due to their ion-exchange and size selectivity capability) [129], photocatalysis [130], thin film technology for applications as membranes and electronic devices [131–135], or pharmaceutical applications [136].

3. Ordered Mesoporous Materials (OMMs)

3.1. History. By the end of the 20th century, zeolites had more than a firm foothold in different fields thanks to their exceptional properties, but unfortunately they were not devoid problems. Since most zeolites are synthesized by means of hydrothermal synthesis [34], their crystal size is generally small, typically in the range of a few microns, and even smaller given some experimental conditions. The direct use of this kind of materials in large beds may cause problems like high pressure drops (which can result in explosions) and difficulties in separation and handling. To avoid such problems, pelletized zeolites are widely used in industry. These materials, however, need the use of a binder that might block a significant part of the porosity, which hinders their effectiveness. From a more fundamental perspective, it would be highly attractive to have a material on which to support a catalyst which offers the clear advantage of confinement effect [30], which would result in a system with improved catalytic performance. This confinement effect has already been used with noticeable success in fine chemistry [29], which is why zeolites were initially proposed as supports for such catalysts. However, their maximum pore size corresponding to zeolite-like materials (more precisely, aluminophosphates) is set on 1.23 nm for VPI-5 [137]. This is a disadvantage in itself since the majority of the molecules that react in pharmaceutical chemistry are rather bulky. Thus, the need arose for materials which presented sufficiently large pores while retaining a narrow pore size distribution (PSD) so as to retain the "confinement effect."

From that starting point, scientists around the world dedicated their efforts to come up with strategies to synthesize zeolites which incorporated mesopores so as to improve diffusivity within the zeolite crystals. Coming back to the phenomenon known as "templating" which was described in detail in the previous section, the idea around which the first studies were founded was that quaternary ammonium ions had been by far the most versatile templates for zeolite synthesis, and the length of the alkyl chain linked to the nitrogen had a specific impact on the type of zeolite Tertiary (composite) Building Units formed during hydrothermal treatment. If one of this alkyl functions was substituted by a longer hydrocarbon chain, there might be a chance that the shorter alkyl functions formed the desired TBUs which would organize themselves around the longer alkyl chain, giving rise to a crystalline, porous structure with the properties of zeolites while having significantly higher accessibility. The initial results were not entirely those expected, but a significant turning point in materials science was reached. In 1992, following up on Japanese researchers which hinted at the possibility of the existence of ordered mesoporous phases [138], a research group from Mobil Oil Corp. reported a material which possessed pores which were regularly spaced with a hexagonal array and a size of 3 nm. This material was named MCM-41 (from Mobil Crystalline Material) [4] and the interest it attracted has increased throughout the years after its discovery due to the fact the pore size may be tuned from 1.4 to 10 nm depending on the synthesis conditions [139, 140] and the novel possibilities it brought forth in the fields of catalysis [141], in large molecules separation, or in host-guest reactions [142]. The discovery of the MCM-41 mesoporous silica, and the family of materials derived from it, gave rise to the formation of a new series of materials normally referred to as nanostructured materials or ordered mesoporous materials (OMMs) [143].

All these features have caused a dramatic increase in the research related to this kind of materials [144–156], paying special attention to their use in a wide array of applications. Despite all this potential, the first tests carried out using mesoporous materials in catalytic application were not as promising as expected mainly due to two aspects.

(i) Despite the fact that trivalent ions can be incorporated into these materials by a wide variety of approaches [157], the various catalytic activity assays have demonstrated that the acidity of these sites is lower than those found in materials such as zeolites for hydrogenation reactions [158–161].

(ii) These materials are generally (especially in the case of all-silica materials) rather unstable when undergoing treatment with hot water or steaming [162, 163]. In this respect, the incorporation of aluminium into the framework may help towards its stabilization [164].

These two features derive from the fact that the walls forming the M41s are not crystalline. The silica found forming the walls is very similar to amorphous SiO_2, as several studies have revealed after ^{29}Si Nuclear Magnetic Resonance (NMR) [142], Synchrotron X-Ray Diffraction (XRD) [165], and Raman spectroscopy [163]. As a result, and as we will explore in the following section, important efforts have been dedicated to the preparation of mesoporous materials which possess skeletal walls with as crystalline and ordered a structure as possible [166], so that the resulting materials have higher acidity, higher resistance to steaming, and easier handling.

At this point, it becomes critical to discuss one point on which rests the very title of this review paper, even if it is just for clarification purposes. Despite the clear mention to "nanoporous" in the keywords, no mention of such a term has been hitherto made. In order to refer to this point we should briefly consider how materials are classified according to

their porosity, or more precisely, according to their pore size. For many decades the pores were divided into micropores (diameter smaller than 2 nm), mesopores (diameter between 2 and 50 nm), and macropores (diameter larger than 50 nm), according to the IUPAC classification [167, 168], which was established as a means to distinguish between the three different adsorption mechanisms that affect the different pores of a solid: volume filling of the porosity by molecules with size similar to the pore size (micropores), capillary condensation (mesopores), and unenhanced adsorption (macropores). While the motivation for establishing the limits for each class of pores is perfectly clear, with the establishing of nanoscience and nanotechnology as disciplines in their own right, to some scientists using the prefix *micro-* to describe something whose size lies in the nanoscale was not strictly correct. Recently, Mays [169] proposed a new way to classify the pores following the guidelines of the Bureau International des Poids et Mesures under Le Système International d'Unités (SI) [170] in order to come up with a more comprehensive nomenclature for pore size (Figure 5).

If we consider the materials that we have described so far (zeolites and ordered mesoporous materials), they both fit in the "nanoporous" materials description according to Mays, even if according to the IUPAC classification they are microporous and mesoporous solids, respectively. As it will be illustrated throughout this review, the vast majority of the materials that will be discussed will fall in the "nanoporous" and "micro/mesoporous" category, inasmuch as a few of them will also possess a porosity which will fit into the "submicroporous" or "macroporous" region. Bearing this in mind, we shall refer to the porosity of the materials using the IUPAC nomenclature, indicating the new nomenclature between parentheses. Thus, zeolites are microporous (subnanoporous) materials, whereas ordered mesoporous materials may possess inter- or even supernanopores.

3.2. Synthesis and Structure. As we discussed with zeolites, there are many hypotheses concerning the mechanism of formation of M41s, or other ordered mesoporous materials synthesized using surfactants. The most relevant mechanisms described to date are

(i) formation mechanism from liquid crystals:

    (1) silicate tubes assembly [171],
    (2) piling of silicate sheets [172],
    (3) "charge density coupling" [173],
    (4) "folded sheets" [174],
    (5) "silicatropic liquid crystals" [175],
    (6) silicate tubes aggregates [176],

(ii) formation mechanism based on electrostatic interactions [177],

(iii) formation mechanism based on hydrogen-bond interactions [178].

Despite the large variety of mechanisms that have been proposed to explain the formation of these materials, and even from numerous recent experiments carried out by Electronic Paramagnetic Resonance [179, 180] and measurements made with probe molecules [181], it has become clear that, as it happened with zeolites, the interaction between the inorganic precursor and the template molecule is the key factor to control the mesostructure of the final material. Nevertheless, the exact stage at which these interactions come into play is still under debate and seems to largely depend on the synthesis conditions. The mechanisms that have been proposed thus far have hitherto failed to provide scientists with a clear and definite answer.

As a very illustrative example, we will describe in detail the mechanism proposed by Firouzi and co-workers [175], by which the formation of M41 materials consists of the self-assembly of silicatropic liquid crystals which are formed in the synthesis solution when oligomeric silica units precipitate on the surfactant micelles, as indicated in Figure 6. Note that in the synthesis of ordered mesoporous materials the micellar ordering of the surfactant employed will depend mainly on the synthesis conditions used, and thus the composition of the synthesis solution, as well as with zeolites, is a parameter of utmost importance. Reference [175] shows this in an excellent way by representing the mineralising agent (NaOH)-silica source (tetraethylorth osilicate (TEOS))-surfactant (cetyltrimethylammonium bromide) ternary phase diagram for a given water/SiO_2 ratio.

The mechanism may be divided into the following stages.

(a) Dissolution of organic and inorganic precursors: depending on the surfactant concentration, the starting organic precursor will consist in micelles with different geometries that will be in dynamic equilibrium with individual surfactant molecules. Dissolution of the inorganic precursor consists mainly of silicate anions with different charges.

(b) When the two solutions are mixed, the silicate oligomers exchange with different anions to form organic-inorganic hybrids, with a structure that may be different to that of the organic precursor micelles.

(c) Multidentate interactions between the silicate oligomers and the surfactant molecules take place, giving rise to the screening of the electrostatic double-layer repulsion forces. This causes the self-assembly of the silicatropic liquid crystal mesophases.

From a purely synthetic point of view, the principle is the same as with zeolites: the key idea is to organize the inorganic oxide species around a template which will give the material its final structure. A representative synthesis would be that of MCM-41 [5], in which the template (cetyltrimethylammonium bromide, commonly referred to as (CTAB)) is dissolved in an appropriate solvent (water) at a given pH, which should be carefully selected in order to control the hydrolysis/dissolution and condensation of the silica precursors. Thus, during the hydrothermal treatment silica precipitates around the surfactant molecules, giving rise to the well-known MCM-41 structure (Figure 7). Removal of the template by calcination yields the final mesoporous (internanoporous) material.

FIGURE 5: New pore size classification as compared with the current IUPAC nomenclature (top). Adapted from [169].
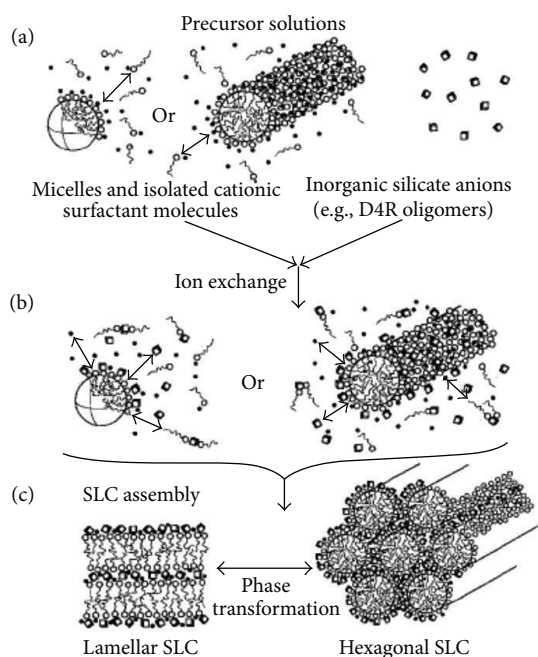

FIGURE 6: Schematic diagram of the cooperative organization of silicate-surfactant mesophases. Taken from [175].

The discovery of MCM-41 together with a family of new mesoporous molecular sieves obtained by what the authors called a liquid-crystal templating mechanism was a significant leap in materials science for it effectively filled the existing gap between microporous (subnanoporous-internanoporous) and macroporous (upper half of super-nanoporous and beyond). This motivated several research groups worldwide to dedicate outstanding research efforts towards the synthesis of novel mesoporous silicates by modifying the synthesis conditions such as pH, hydrothermal conditions, or the use of surfactants of very different natures (Figure 8). This gave rise to the discovery of a wide array of mesoporous material families, such as SBA [182, 183], FDU [184–186], AMS [187, 188], MSU [189, 190], KIT [191, 192], or TUD [193] to name just a few examples. This wide variety of materials, each one with their own characteristic structure and framework resulted from the numerous synthetic parameters that could be fine tuned, such as the reaction pH (ordered mesoporous materials have been synthesized both under acidic and basic conditions), the synthesis temperature, the hydrothermal synthesis conditions, the nature and concentration of template, and even the template removal process selected [194]. Some comments should be made concerning these aspects such as the following.

(i) Even though Mobil scientists claimed that they used hydrothermal synthesis for the preparation of MCM-41, the differences between "traditional" hydrothermal synthesis (i.e., the one used for zeolite synthesis) and the "new" one are (1) lower temperatures and narrow temperature range, (2) significantly higher formation rate in the case of ordered mesoporous materials, and (3) while zeolites require water as solvent in their synthesis, several reports have successfully prepared ordered mesoporous materials in nonaqueous media by different strategies [195–198].

(ii) In order to improve the quality or thermal stability of ordered mesoporous materials, several postsynthesis treatments have been devised. For instance, submitting an MCM-41 material with $AlCl_3$ vapour [199] will result in improved mechanical and hydrothermal properties, whereas a treatment with ethanol vapour [200] or gaseous ammonia [201] improves the structural ordering. Xia and Mokaya reported a method to restructure activated MCM-41 using it as the "silica source" in a synthesis gel consisting of a templating agent (CTAB), TMA-OH, and water [202]. After the secondary hydrothermal treatment, the resulting material exhibits excellent hydrothermal stability, which is attributed to the improvement of condensation degrees of silicates. Another postsynthesis treatment that has proven its efficiency in improving the regularity of mesoporous materials is recrystallization [203]. The process of recrystallization is carried out using the as-synthesized powder samples without washing, which are placed in distilled/deionized water at 100–150°C for periods
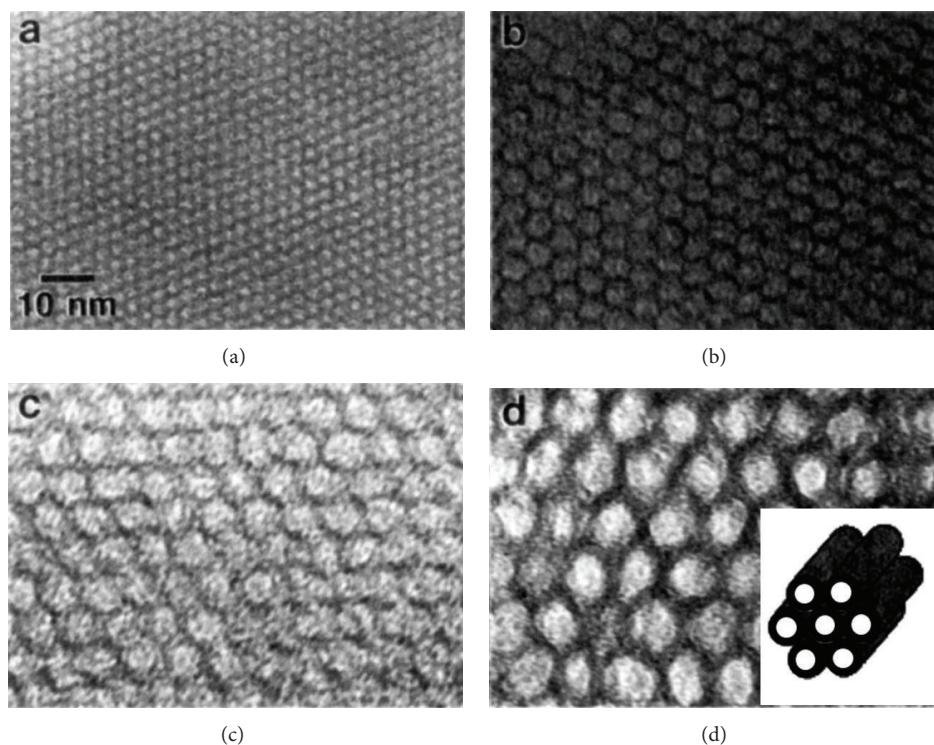
FIGURE 7: Different MCM-41 materials with pore sizes ranging from (a) 20, (b) 40, (c) 65, to (d) 100 Å. The inset in the lower right-hand corner shows a schematic representation of the porous array of MCM-41. Adapted from [5].

between 1 and 7 days. The quality (ordering, thermal stability, etc.) has been improved for most materials, sometimes accompanied with the enlargement of pore sizes.

(iii) In order to control the final structure of the materials, the control must be carried out on the mesocale, which includes the mesophases formed by the surfactants employed, as well as the resulting pore size and pore wall thickness. In this respect, parameter such as the critical micellar concentration, the phase diagram of the given surfactant in the reaction medium, or the hydrophilic/hydrophobic volume ratio of the surfactant must be taken into account. This in turn will result in the formation of 2D (e.g., space groups *p6mm* or *cmm*), 3D (e.g., space groups *Fm3m, Im3m, Pm3m,* or *Fd3m*) or lamellar mesostructures.

Although a large number of methods have been reported to prepare all-silica and silica-rich mesostructures (see [194] and references therein), the preparation of nonsilica mesoporous materials is more challenging. The hydrolysis and condensation of silica precursors (usually tetraethyl orthosilicate (TEOS) in water) can be controlled thoroughly, with the resulting silicas being relatively thermally stable during calcination, the hydrolysis and condensation of nonsilica precursors (e.g., metal alkoxides) are generally difficult to control [204]. In this respect, the beginning of the 21st century gave way to a new array of synthetic methods which greatly broadened the possibilities even more. The use of surfactants (either ionic or nonionic) continued, often

referred to as "soft" templating, while a new method known as "hard" templating offered the possibility of preparing novel mesostructured materials [205, 206].

The soft templating method refers to those strategies developed for the synthesis of ordered mesoporous materials using species which may be removed either by calcination [208] or by solvent extraction [209]. The preparation of ordered mesostructured metal oxides using soft templates was first reported shortly after the synthesis of MCM-41 [177]. Antonelli and Ying reported a "ligand assisted" methodology [208] that was firstly used for the preparation of mesoporous TiO_2, which was then later adopted for the preparation of other mesoporous metal oxides such as Nb_2O_5, Ta_2O_5, VO_x, and ZrO_2 [210–214]. These syntheses relied on the cocondensation of species with opposite charges or species with similar charges mediated by the intercalation of counter ions. Another widely used method in the preparation of mesoporous oxides is Evaporation Induced Self-Assembly (EISA), first reported by Brinker and coworkers [215] which was later used in several research groups worldwide, such as the Stucky, Antonietti, or Sanchez groups [195, 216–218]. By means of in situ small angle X-ray scattering (SAXS), wide angle X-ray scattering (WAXS), and Fourier transform infrared (FTIR) spectroscopy it has been possible to investigate the mechanism involving the EISA process and to divide this process into three steps: (a) preparation of stable solutions containing the templating agent (surfactant) and the inorganic precursors at the appropriate stoichiometry; (b) evaporation induced self-assembly associated with dip-coating. Evaporation of the solvent over time induces

Sodium dodecyl sulphate
(SDS)

Poly(sodium 4-styrenesulfonate)
(PSS)

(a)

3-((3-cholamidopropyl)
dimethylammonium)-1-propanesulfonate
(CHAPS)

(b)

$x : y : z = 20 : 70 : 20$

Pluronic P-123
(P-123)

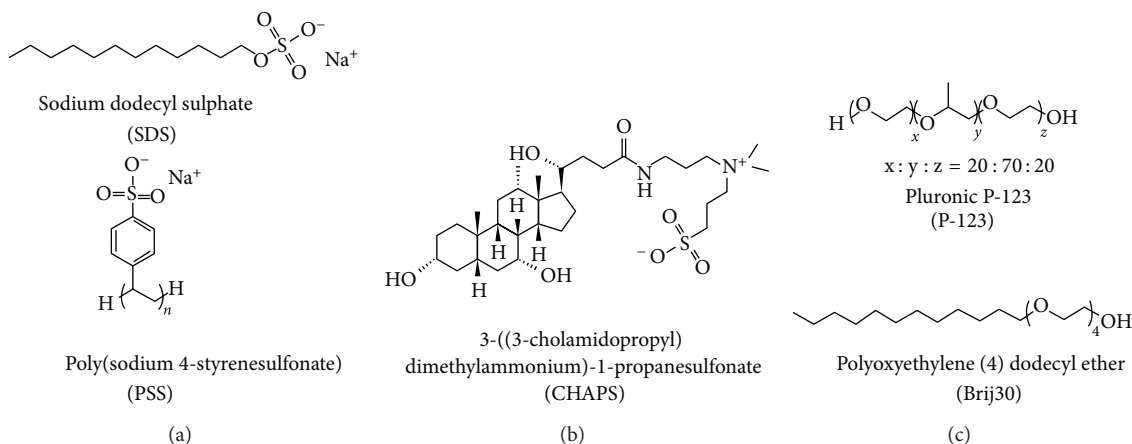Polyoxyethylene (4) dodecyl ether
(Brij30)

(c)

FIGURE 8: Some examples of surfactants of different chemical nature. Left: ionic surfactants (CTAB would belong to this category); Center: zwitterionic surfactant; right: nonionic surfactants. For an extensive list of surfactants commonly used in mesoporous materials synthesis please refer to the excellent review by Wan and Zhao [194].

the progressive concentration of inorganic precursors into a homogeneous, flexible, and poorly condensed network surrounding the surfactant mesophase; (c) sample treatment involving pre-consolidation, template removal, and network crystallization. In this way, complex metal oxide nanocrystalline films (e.g., $SrTiO_3$, $MgTa_2O_6$) may be obtained [219]. These two approaches have been widely used for the synthesis of a very wide array of mesoporous oxides and have been perfected for the preparation of mesoporous monoliths through simple lyotropic and microemulsion liquid crystal templates (see [220–223]) and references therein).

Unlike the soft templating method, in which the surfactant arranges itself during the synthesis process in order to give rise to the desired structure if the appropriate synthesis conditions are met, the hard templating method relies on the use of preshaped solid forms as templates, which, upon deposition of the desired oxide species and removal of the "mold" gives rise to the final desired material. This method may be found in the literature with other names such as nanocasting [205, 225, 226], exotemplating [227], or repeated templating method [207]. Porous Al_2O_3 supports prepared by anodic oxidation (AAO or anodized aluminium oxide) [228, 229] were used initially as a mold to prepare carbons, metals, or other nanostructures by a variety of techniques such as electrodeposition [230], Chemical Vapour Deposition (CVD) [231–233], Plasma-Enhanced Chemical Vapour Deposition (PE-CVD) [234], or Atomic Layer Deposition [235]. The resulting materials have a pore size ranging from a few nanometers to several tens of nanometers. Based on this methodology, the discovery or ordered mesoporous materials provided a new set of templates or scaffolds on which to open up new avenues of research. To name just a simple yet very illustrative example, Ryoo and coworkers reported the synthesis of a 3D mesoporous carbon (CMK-1) and a mesoporous Pt network using MCM-48 as template [236–240]. A scheme depicting the general procedure of preparation of mesoporous materials by hard templating is illustrated in Figure 9.

Porous matrix
(e.g., SBA-15
silica)

Infiltration
of precursor

Conversion
into solid
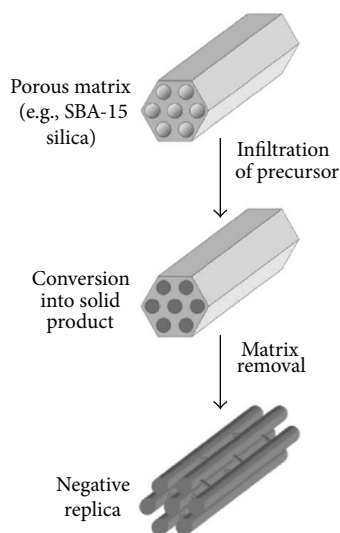product

Matrix
removal

Negative
replica

FIGURE 9: A schematic diagram of mesoporous material synthesis by hard templating synthesis using SBA-15. Taken from [207].

In this particular example, the silica mesopores are first infiltrated with a precursor solution of the species that will give rise to the negative replica of the material. The precursor is converted to a solid by reduction or decomposition inside the pores. Then the mesoporous silica template is removed using a suitable solution (aqueous NaOH or HF are amongst the most popular for silica hard templates), and after washing, a material replicating the mesostructure of the hard template is obtained. The presence of disordered micropores between the 1D mesopores of SBA-15 ensures that the replica carbon or metal oxide nanowire arrays are connected by bridges so as to form mesopores (a good example is the material known as CMK-3) [242]. The use of MCM-41 would, in this case, only render carbon nanowires [237]. Mesoporous materials (be it either silica or carbon) have both been used as hard templates for the development of ordered mesoporous metal oxides. In

this sense, the first porous metal oxide with high crystallinity was reported in 2003 [243], when a functionalized SBA-15 was used as hard template for the loading of potassium dichromate, which upon thermal treatment and template removal gave rise to an ordered mesoporous Cr_2O_3. Other recent examples include mesoporous WO_3 and α-Fe_2O_3 [244, 245].

In the hard templating protocol, it is not straightforward to fill a mesoporous silica template completely, because there are complex interactions between the silica and filtrated ion precursor, which include Coulombic interactions, hydrogen bonding, coordinating interactions, and van der Waals interactions [205]. Therefore, different methods have been developed to improve the filling of the mesostructure and minimize the loading outside pores, which will rise to an amorphous oxide. Metal ion precursors can interact with the fresh silica template through weak Coulombic interactions with surface silanol groups. In order to maximize the interaction between the metal oxide precursor and the template, thus optimizing the amount of metal precursor for the preparation of a good negative replica, the first attempts focused on the creation of as many silanol groups as possible [247]. More recent efforts have established that mesoporous materials may be functionalized (either by one-pot preparation, post-synthesis grafting or tethering) in order to introduce organic groups such as amine or olefins that in turn lead to a strong interaction between the organic group and metal ion precursor, thus improving the loading of metal ion precursor [248].

Ordered mesoporous solids may also be prepared by the hard templating method without the template having to undergo surface functionalization, following alternative methodologies such as the dual solvent method, solvent evaporation method, solid-liquid method, combustion method, or the impregnation-precipitation-calcination method. In the dual solvent method a suspension of the hard template in a highly hydrophobic solvent (e.g., hexane) is mixed with a concentrated aqueous solution of the oxide precursor. Generally, the solution volume is equal to the pore volume of the template in order to maximize the impregnation quantity and prevent the growth of solid phase on the outer surface of the hard template [250]. The driving force for the precursor ions to enter the porous template is the difference in polarity of both solvents. In the case of the solvent evaporation method, a solution of the oxide precursor in a volatile solvent is mixed with the template. The capillary condensation during the slow evaporation of the solvent is the cause for the ions to migrate into the pores [251]. In the sold-liquid method, a solid precursor with a sufficiently low melting point is selected. The oxide precursor is ground with a mesoporous silica template, and slowly diffuses into the pores of silica after melting when the mixed solid is heated to a temperature above the melting point of the precursor [252]. The impregnation-precipitation-calcination method has been successfully applied in the preparation of mesoporous CeO_2 [253], Co_3O_4, and NiO [254]. Other methods for the synthesis of ordered mesoporous oxides include the formation of a carbon "scaffold" to reinforce the formation of the porous mesostructure in what is known as the "reinforced" method, which has been
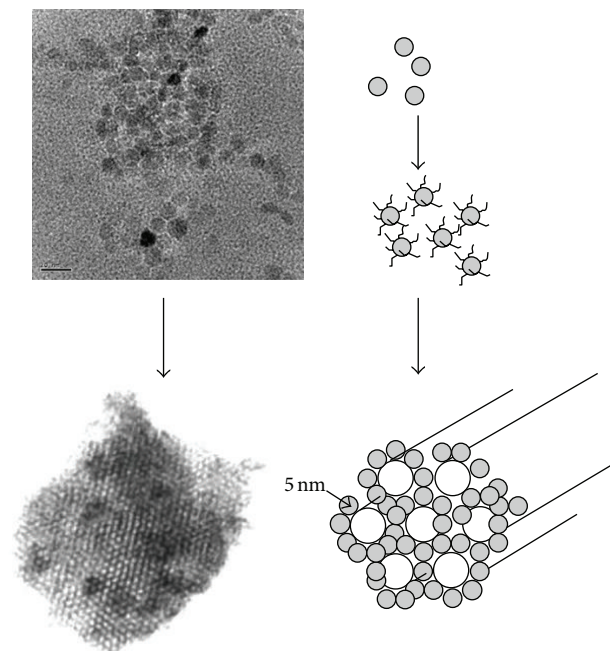

Figure 10: CeO_2 nanoparticle self-assembly methodology for the synthesis of ordered mesoporous CeO_2. Adapted from [224].

successfully used in the synthesis of different mesoporous oxides such as Ta_2O_5, Al_2TiO_5, $TiZr_2O_6$, or Nb_2O_5 [255]. The synthesis of more complicated (or uncommon) metal oxides with an ordered mesoporous structure has also been attempted by postsynthesis methods. For instance, Ren and coworkers demonstrated that CoO, Mn_3O_4 and Cu-Cu_2O may be obtained by partial reduction of Co_3O_4, MnO_2, and CuO, respectively [256]. This solid-solid interconversion method has been also successfully applied to other metal oxides such as Fe_3O_4 or γ-Fe_2O_3 prepared from α-Fe_2O_3 by partial reduction or oxidation [257]. Following the solid-solid conversion method, postsynthesis modification of the prepared materials may be achieved, as evidenced by the preparation of mesoporous lithium-manganese and lithium-copper spinels from the corresponding transition metal oxides [258].

The preparation of mesoporous oxides by the soft templating method involves different reactions such as the hydrolysis of the inorganic precursors, condensation of the inorganic oxide ions, and self-assembly with the template to give rise to the final mesostructure. All these steps have proven to be highly sensitive to the reaction conditions. If the self-assembly processing is based on the arrangement of already formed monodisperse nanoparticles around the template, the process will be less sensitive to the variable reaction conditions [224]. Corma and coworkers have successfully applied this principle for the preparation of ordered mesoporous CeO_2 and ZrO_2 using Pluronic P123 as the template, as shown in Figure 10 [260, 261].

3.3. Applications of Ordered Mesoporous Materials. Despite the fact that ordered mesoporous materials were firstly envisioned as a means to overcome the limitations of zeolites
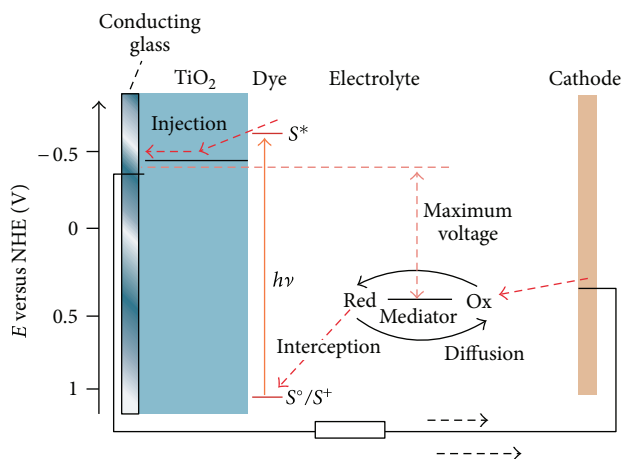
FIGURE 11: Schematic illustration for the operation of a dye-sensitized solar cell (DSSC). Taken from [241].

when operating in large packed beds, the low crystallinity of the walls of the resulting materials resulted in a significantly poorer performance than the one intended. Several groups attempted to improve this aspect by a variety of techniques, such as the development of benzene-silica hybrids to improve wall crystallinity [166], or the use of the so-called zeolite seeds as inorganic precursors to give rise to mesoporous materials with enhanced hydrothermal stability [263, 264]. Despite all these efforts, ordered mesoporous materials have not been able to substitute zeolite in refinery plants since they are either not hydrothermally stable at high temperatures or those which are stable under severe conditions are too expensive to obtain and thus are not as cost effective as zeolites. Nevertheless, research on ordered mesoporous materials has opened up many pathways which have led to the development of a vast array of single and mixed-metal oxide materials with a large selection of porous structures and pore sizes, and thus all the applications that will be described here, even if some of them are still in the initial steps, clearly reflect the potential and the impact of this new family of materials which undoubtedly signified a revolution in materials science at the end of the 20th century.

Commercial bulk metal oxides are widely available and used extensively in catalysis, sensing, adsorption and separation, purification, energy conversion and storage, and so forth [266]. However, the surface area, pore size, porous structure, and particle size may have a large impact on such applications. Ordered mesoporous materials, with their higher surface areas and ordered pore structures, should demonstrate better performance. Different applications of ordered mesoporous inorganic oxides will be highlighted in this section to illustrate their enormous potential.

In the field of solar cells, Dye Sensitized Solar Cells (DSSCs) use a light absorbing dye which transfers the electrons to a cathode by means of an electrochemical reaction, which in turn gives a current (Figure 11). In this respect, mesoporous materials with photocatalytic activity such as mesostructured TiO_2 may play a very important role [241,

267, 268]. In DSSCs, TiO_2 films are used to absorb and host the dye, which is attached to the anode, typically made of transparent conductive glass of the indium-tin oxide (ITO) type [269]. In this respect, TiO_2 nanoparticles with random orientation have a large number of particle boundaries which have a detrimental, which may limit the rate of electron transfer out of the active layer. Thus, the use of highly crystalline mesoporous metal oxides is a subject of great interest, as several authors have reported [260, 270–275]. In this respect, SnO_2 has higher electron mobility and more positive conduction band edge position than TiO_2, both of which could allow a DSSC with a structured SnO_2 photo anode to demonstrate superior performance than a TiO_2 photoanode-based cell. Ordered mesoporous SnO_2 with a tridimensional cubic mesostructure, high surface area, and crystalline framework was synthesized following the hard templating method using KIT-6. The resulting DSSC showed an improved open-circuit voltage, short-circuit current, resulting in a significant improvement of the energy conversion efficiency [276].

Mesoporous metal oxides are also very attractive materials for the construction of electrode materials for lithium ion batteries. The domains of mesoporous metal oxides are micron-sized, thus the fabrication of composite electrodes should be similar to the synthesis of dense micron-sized particles, thus resulting in a similar packing density (i.e. no efficiency loss). The contact between domains is sufficiently good to ensure an efficient electron transport. The thin walls of the oxide framework (in the range of a few nanometers) result in short diffusional pathways for the lithium ions on intercalation. Moreover, thanks to the high surface area that ordered mesoporous materials exhibit and the hydrophilic nature of inorganic oxides, flooding of the pores by the electrolyte will result to enhanced electrode reaction kinetics (this benefit also applies in the case of the previous advantage). Finally, the ordered mesopores have approximately the same dimensions as the walls, thus the lithium ion transportation is practically identical everywhere within the pore and within the wall. Such an ordered structure ensures that a mesopore/wall size may be fine tuned so as to permit efficient Li^+ transport. In this way, it should be possible to obtain an electrode displaying the optimum balance between high rate performance and high volumetric capacity. In this respect, different ordered mesoporous metal oxides have been reported for their use as electrode materials. Cathodes include different Li, Co, Ni, and Mn-based spinels [251, 258] and β-MnO_2 [277, 278]. Anode materials include mesoporous Co_3O_4 [279], Fe_2O_3 [280], MoO_2 [281], NiO [282], SnO_2 [283], and TiO_2 [284].

Another area in which mesoporous materials have been applied with some promise is that of supercapacitors. These materials are of high interest due to their high energy and power density, which in turn bridges the gap between conventional batteries and classical electric capacitors [285]. There are two large groups of electrochemical supercapacitors, namely, double layer and redox supercapacitors. In the former case, the charge is stored in the electrical double layer of each electrode while in the latter there is a degree of intercalation that resembles a battery conformation. In the field of electric
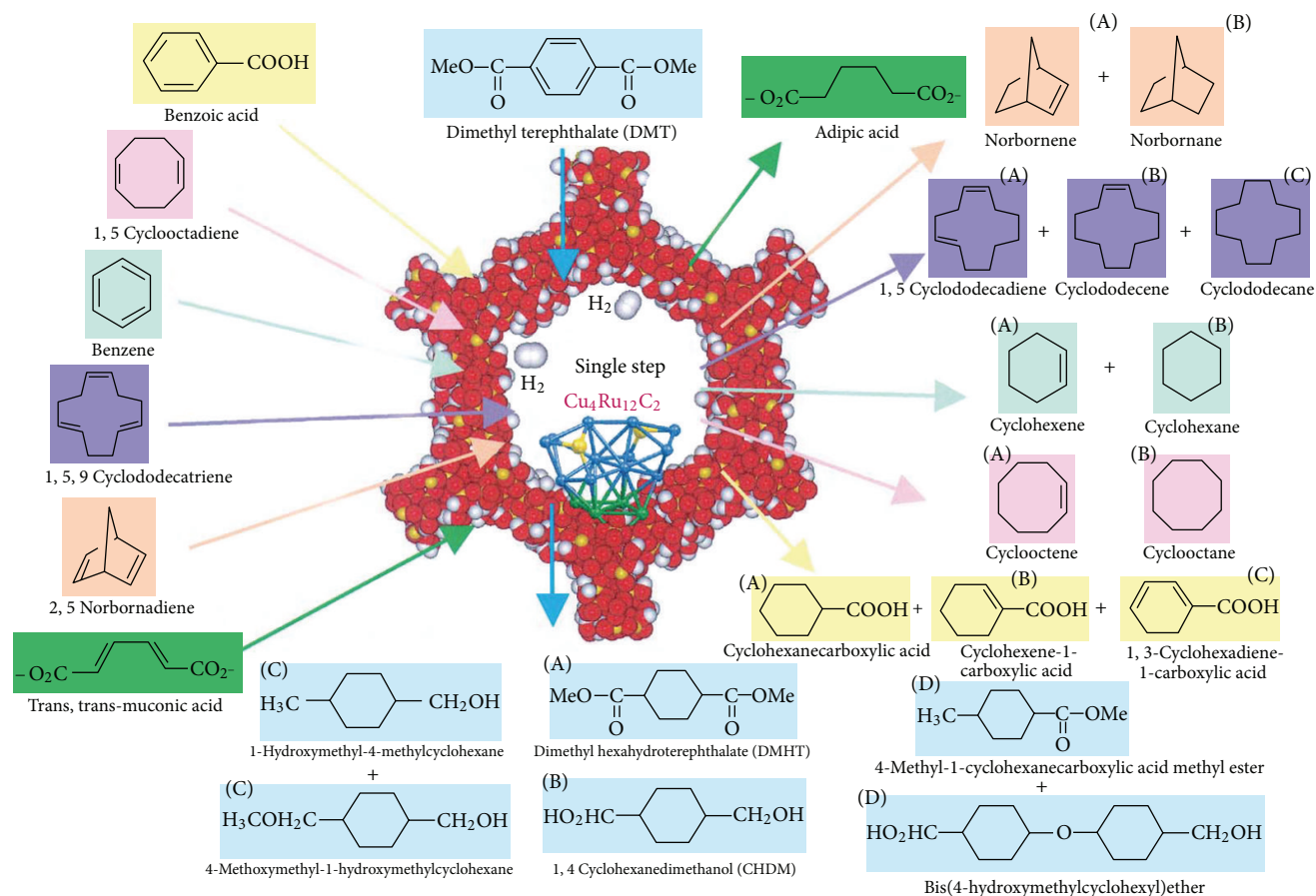
Figure 12: A visual one-shot image of the usefulness of ordered mesoporous silica (MCM-41) used as catalyst support in single-step hydrogenation reactions using a $Cu_4Ru_{12}C_2$ cluster. Taken from [246].

double layer capacitors (EDLCs), materials such as chemical-activated carbon [285–287] or novel forms of carbon such as Zeolite-Templated Carbon (ZTC) [288, 289] have shown great promise as electrode materials. The main advantage of redox supercapacitors is that they possess high energy density, although the values are somewhat distant from conventional batteries. Supercapacitors offer much faster charging than a battery and therefore are envisaged for high power but not energy-demanding applications. Mesoporous metals such as Pt or Ni [290] and metal oxides like TiO_2, Nb_2O_5, Ta_2O_5 [291], MnO_2 [292], and Co_3O_4 [293] have been tested as redox supercapacitor electrodes.

The high internal surface area of mesoporous materials in general and the redox character displayed by some mesoporous metal oxides has been the drive of an enormous research effort to prove the efficiency of these materials in a very wide array of reactions. Even though we will just address a few examples due to the general scope of this review, any readers interested in this topic are recommended to read the excellent paper by Johnson [246] which provides a very clear view of the usefulness of ordered mesoporous materials as molecular cluster (i.e., nanoparticulate catalyst) supports in an ample array of reactions (see Figure 12).

The high accessibility of ordered mesoporous materials also makes them ideal candidates for metallic nanoparticles, as we have shown in a number of papers which clearly present the potential of these materials in different reactions of significant applied interest [294, 295]. Just to name a few specific examples of specific applications in which ordered mesoporous materials have been successfully applied include redox reaction such as CO oxidation [296, 297], methanol decomposition [298], or N_2 fixation [299], solid acid catalysis processes (e.g., the loading of Keggin-type structures on mesoporous materials for the decomposition of N_2O) [300, 301], and photocatalysis reactions for the preparation of self-cleaning surfaces [302] or the photoelectrolysis of water (i.e., water splitting) [303].

The use of metal oxide-based sensors is of high current interest due to their robustness, cost efficiency, and excellent sensing capabilities. When a chemical reaction takes place on a semiconductor surface, the electron transfer between the gas molecules and semiconducting material surface will result in a quantifiable variation of a measurable parameter such as electric conductivity/resistivity (Figure 13), thus the gas concentration can be precisely determined. Since gas sensing involves adsorption and to some degree of reaction

(a)

Sensing layer

Pt electrode

Substrate
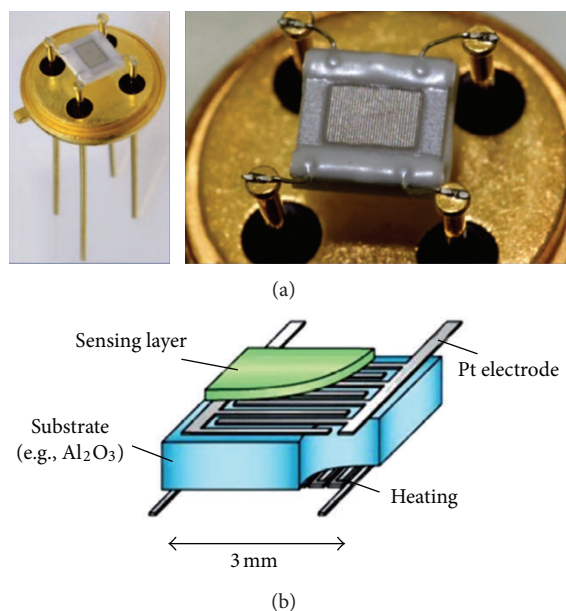(e.g., Al$_2$O$_3$)

Heating

3 mm

(b)

FIGURE 13: Images (top) and schematics (bottom) of an example sensor substrate (UST Umweltsensortechnik GmbH, Germany). Taken from [249].

at the solid-gas interphase, one of the main parameters determining the sensitivity of a semiconductor sensor is its surface area. If this is coupled with the improved diffusional properties of mesoporous materials, the development of ordered semiconductor mesoporous metal oxides is also a field which has attracted great attention [304]. Thus, ordered mesoporous SnO$_2$ has been synthesized and tested for H$_2$ sensing applications, showing superior performance compared to a conventional sensor, even though the quality of the sensor heavily depended on the specific surface area of the mesoporous material involved [305, 306]. Mesoporous WO$_3$ prepared by hard templating has been used for the sensing of NO$_2$, showing that the template used may have a significant influence on the quality of the resulting sensor [307, 308]. Tiemann and coworkers reported the synthesis of mesoporous ZnO and Co$_3$O$_4$ for CO and NO$_2$ sensor development [249, 309], while Prim and coworkers recently reported the use of CaO-loaded mesoporous In$_2$O$_3$ for CO$_2$ sensing applications [310].

Despite all the applications that have been mentioned in this review, in which ordered mesoporous materials have clearly shown their potential, the industrial implementation is still a few years since one of the main obstacles this new family of solids must overcome is the cost effectiveness of the resulting materials/catalysts, since the preparation of high quality ordered mesoporous materials for user-end applications requires a control of the synthesis conditions that may be still too demanding for its inclusion in the industrial horizon. Despite their shortcomings, ordered mesoporous materials deserve an outstanding merit for the new perspective they brought into materials, which opened up new avenues which have resulted in an ever widening array of applications.

4. Hierarchical Materials

4.1. History. Throughout this paper we have dealt with materials which were either microporous (subnanoporous) or mesoporous (inter- or supernanoporous), with either a crystalline structure or formed by amorphous skeletal walls which possessed regular porous ordering. As we previously mentioned, one of the "philosopher's stone" in materials science and catalysis would be the development of zeolites which retained their outstanding catalytic activity while being able to process larger molecules or to reduce the diffusional limitations in catalyst beds due to their small pore size. In this specific instance is where hierarchical materials fit the requirements perfectly. The Oxford English Dictionary describes the term "hierarchical" as "belonging or according to a regular gradation of orders, classes, or ranks." This, applied to porous materials usually refers to a type of materials possessing pores (preferentially regular) of different categories, which are effectively combined in a material with superior properties. In principle, the term hierarchical should refer to materials which have different types of ordered porosity, whose sizes lie in the different pore size regions (micro-, meso-, macroporous or sub-, inter- and supernanoporous), but the term is also used for materials in which some of the porosity may not be perfectly ordered, but which nonetheless present a certain degree of structuring. In short, in a hierarchical material each level of porosity in the structure fulfills a distinct complementary task: the micropores hold catalytically active sites and adsorb smaller molecules, whose access is facilitated by the newly introduced mesoporosity which can also adsorb larger molecules, with the enhanced diffusion through the network introduced by the macroporosity. Just to give an account of the importance of hierarchical materials, the journal Science recently appointed the development of such materials as one of the runners-up for the "Scientific Breakthrough of 2012" [311]. From this review, it should become quite clear that if there is one type of materials that should greatly benefit from the synthesis of hierarchical structures is zeolites, since the suboptimal use of this class of aluminosilicates is brought forth by the limited access to, and/or diffusional hindrances within, their microporosity. It must be noted that, being a significantly novel family of materials, literature and especially applications for hierarchical materials is still "under development" and thus the section corresponding to *applications* will be limited to those detailed in some of the referenced publications.

4.2. Synthesis and Structure. There are essentially three ways to create materials with hierarchical porosity: to take a porous material and create a different family of pores which belong to a different category (top-down techniques), to build a material from scratch designing the appropriate template or a selection of templates (bottom-up techniques), or to use a combination of both. The earlier works dealing with bottom-up techniques described the development of microporous-mesoporous composites [312, 313] in which smaller building units such as for example nanosized zeolite crystals [263, 264, 314] may be employed as the primary building blocks, which
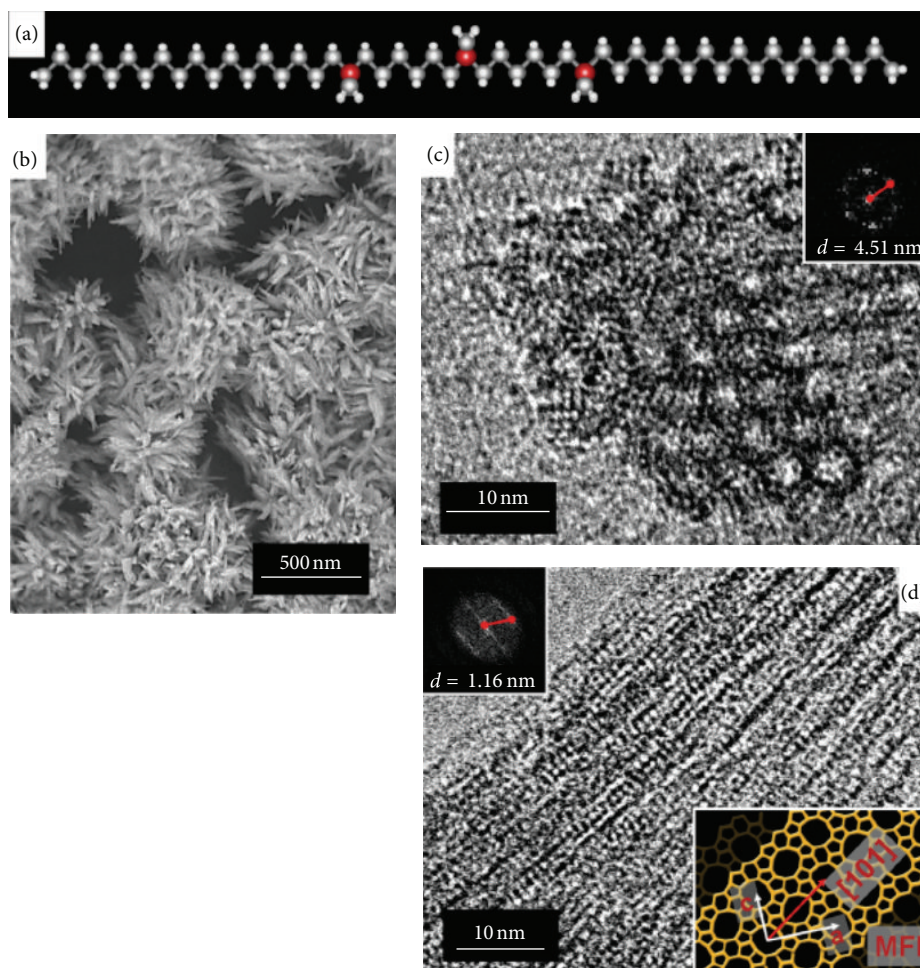
FIGURE 14: (a) 18-N$_3$-18 surfactant (white spheres, hydrogen; gray spheres, carbon; red spheres, nitrogen) used in the synthesis of a hierarchical material with zeolite walls (b) SEM, and (c, d) TEM images of the resulting material. Insets in (c) and (d) Fourier diffractograms, for structural comparison, an MFI framework model is given in the bottom right inset of (d). Adapted from [259].

upon self-assembly will give rise to the hierarchical structure. Other included the use of a combination of templates, one to create microporosity, the second to create mesoporosity [315]. The most advanced and recent developments in the preparation of hierarchical zeolites and zeolite-like materials were recently reported by the groups of Corma [316] and Ryoo [317] in which they used very sophisticated and elegant templates, the former inspired in the synthesis of silicogermanates using piperidinium-derived salts, which was reported by the authors as a very promising route to direct the synthesis towards zeolites with extra-large pores and to multipores zeolites [318] while the latter elaborated on the development of "bifunctional" templates [259] to prepare a mesoporous molecular sieve (MMS) which possessed walls with a crystalline zeolite structure, as evidenced by a variety of techniques (see Figure 14).

In the case of top-down synthetic routes, they involve a series of postsynthetic treatments of previously formed materials by the removal of framework atoms or delamination. Some classical examples include steam [319], acid [319], or base treatments [262, 320], while more sophisticated

approaches include the use of swelling agents [321, 322], irradiation [323], or strongly oxidative reagents [324]. It should be noted that from a practical point of view, top-down techniques provide the user with added benefits from a HSE (health-safety-environment) and production costs perspective since they do not involve the use of large amounts of costly template(s). From all the top-down techniques which are available nowadays, perhaps one of the earliest ones to be reported was that of base treatment or alkaline leaching, which was first patented by Young in 1967 [325] as a means to improve the performance of mordenite in adsorption and catalysis. From this point on, the strategy known as desilication (removal of silicon species from zeolites by alkaline treatment) has given risen to a large number of publications reporting several types of mesopores developed within zeolitic structures (for a detailed list, please see Table 1 in [262]) (Figure 15).

Another recent development in the preparation of hierarchical materials involves both top-down and bottom-up techniques. Following on a previous work [265] and by means of a combination of soft- and hard-templating techniques,
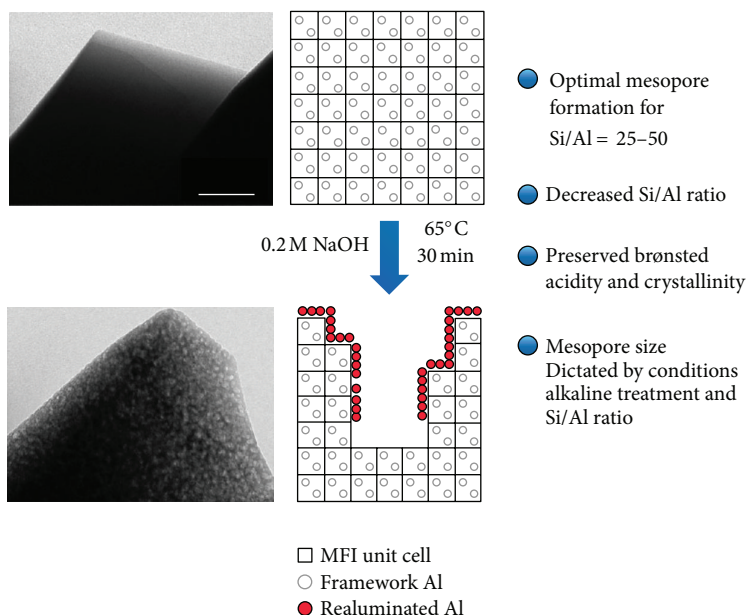
FIGURE 15: Schematic representation of desilication by NaOH treatment of MFI-type zeolites. The images show two MFI zeolite crystals before and after alkaline treatment, respectively. Adapted from [262].
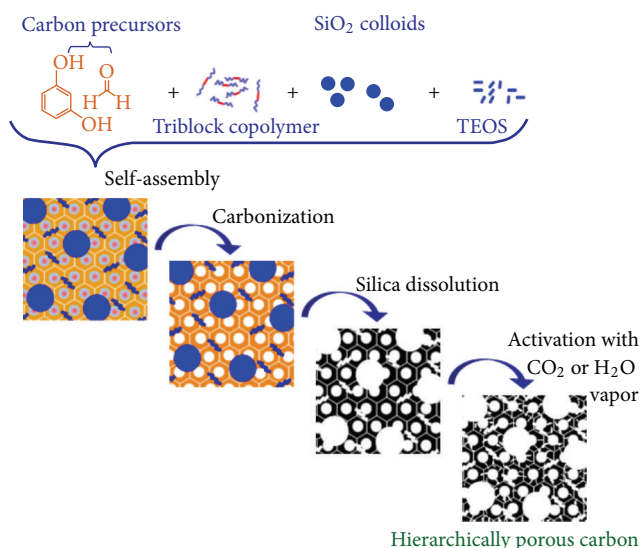

FIGURE 16: Schematic illustration of a combined soft- and hard-templating synthesis of mesoporous carbons subjected to postsynthesis physical activation with CO_2 or H_2O. Taken from [265].

Górka and Jaroniec reported the development of hierarchical carbons showing both microporosity (obtained using a top-down technique such as physical activation of carbon materials) and mesoporosity (obtained using a bottom-up technique such as the soft-templating of silica materials coupled with carbon precursors such as resorcinol and formaldehyde) (Figure 16). The application of soft templating techniques to the development of ordered mesoporous carbons (OMCs) [242] has provided scientists with a powerful methodology to develop a new kind of hierarchical materials.

Concerning the applications of these materials, some recent reviews have already pointed out that hierarchical zeolitic materials can clearly outperform their solely microporous counterparts in different reactions such as isomerization, alkylation, acylation, aromatization, pyrolysis, cracking, and methanol-to-hydrocarbons [326, 327]. Furthermore, some works have also noted that these materials improve the performance of heterogeneous catalysts when used as supports instead of classical zeolites in hydrodesulfuration reactions [328].

5. Conclusions and Outlook

From the first porous carbon that was used by man, it is clear that we have taken many and very significant steps towards the formation of ordered porous materials which combine different pore architectures with tunable pore sizes (and shapes), which can be effectively combined to form what we could call "materials-on-demand." It is clear that materials science has evolved noticeably since the discovery of zeolites and has found a way to evolve in order to create larger pores when diffusional limitations were the main hurdle to be overcome, giving rise to OMMs. Then, as hydrothermal stability became a serious issue, scientists developed OMMs with highly crystalline walls which showed very high thermal and hydrothermal stability. The last (surely not final) frontier that has recently been breached is that of combining different types of pores into one single material which has given rise to the family known as hierarchical materials. In this respect, great advances have been made in the development of different hierarchical materials such as carbons, silicogermanates, and especially zeolites. In the last years major progress has been achieved in the synthesis and

application of mesoporous zeolites prepared by a variety of techniques, both in terms of reported benefits in catalyzed reactions and general understanding of the synthesis mechanism. The industrial application of these exciting materials should be a matter to be solved in the coming years, that is, if they are not being already applied in a medium-to-large scale already. It should be noted that the materials which have the best outlook towards industrial implementation seem to be hierarchical zeolites synthesized with top-down techniques since they do not require the use of large amounts of sophisticated templates which hitherto need to be custom-made. Nevertheless, some fundamental issues concerning the mesopore formation by desilication still need to be fully addressed. Although some general rules and guidelines have been devised, the process of mesopore formation on a molecular level in this type of materials is still unclear. In any case, the next step towards industrial incorporation of these materials was already undertaken by Groen and coworkers [329], which is the scaling-up of the synthesis process to obtain large batches of mesoporous zeolites. At this point, the necessary shift in catalyst design is to shape the obtained materials into pellets or other types of large structure for their easy handling. This will enable the detailed study of these new materials as an applied hierarchical catalyst. The crucial aspect will like in the answering to the question whether the structure-property-function relationships obtained for powders synthesized in the laboratory apply also for shaped mesoporous zeolites.

Acknowledgments

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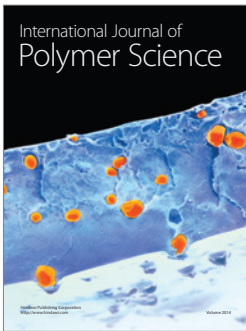
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