Direct Synthesis of Functional Zeolitic Materials

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Recently, the direct synthesis of zeolitic materials has received much attention because several well-defined functionalities have been introduced in those materials by “one-pot” methodologies. The rationalization of the physics and chemistry of the processes involved in the zeolite growth has allowed the direct preparation of different functional molecular sieves with unique properties and potential applicability in industry. In the present paper, the “one-pot" preparations of metal-containing zeolites (both in framework and extra-framework positions), hybrid organic-inorganic molecular sieves, hierarchical microporous mesoporous zeotypes, nanosheets, nanozeolites, or template-free molecular sieves are intensively evaluated.

1. Introduction

Zeolites are one of the most significant materials in chemistry, their application as catalysts being especially important in relevant industrial processes [1]. Indeed, zeolites have been exploited as industrial catalysts in several petroleum derived chemical processes (e.g., catalytic cracking, hydrocracking, isomerization, disproportionation, aromatics alkylation, methanol to gasoline, dewaxing, etc.) and fine chemical processes (selective oxidation of olefins or fragrance synthesis, etc.) [2]. This large industrial applicability of zeolites can be related to the exceptional versatility that those materials offer as solids whose structure and surface properties can be tailored easily. In this sense, zeolites are microporous materials with regular pores and cavities of molecular dimensions (3–15 Å) formed by heteroatoms in tetrahedral coordination (primary Si and Al) connected through oxygen atoms [3]. Their chemical composition can be tuned by introducing other heteroatoms (Ti, Sn, Fe, Cu, Co etc.), both in framework or extra-framework positions, and consequently, the nature of the catalytic active sites (acid-base or redox centers). Moreover, the accessibility to those catalytic active sites and the molecular traffic within the zeolite can be controlled by varying the size of the pores, the number of different openings through which molecules can circulate (mono-, bi-, or three-dimensional zeolites), and also tuning the zeolite crystal size (which typically ranges from 20 nm to 5 μm). Those “tailor-made” physicochemical abilities, together with their high hydrothermal stability and “non toxic” character, have allowed their wide application in industry.

The design and synthesis of a zeolite with the adequate physicochemical properties for their application in an industrial chemical process have to be rationalized keeping in mind not only the scientific requirements, but also the overall economic cost of its manufacture. In this sense, the direct or “one-pot” synthesis of functional microporous materials would offer attractive advantages versus “multistep” preparations, for example, as significant cost savings could be accomplished by reducing the number of steps required in the catalyst synthesis. The control over the variables that govern and direct the “one-pot” synthesis towards the microporous material with customized properties is a very challenging and industrially relevant task.

In the last years, great efforts have been made on the direct preparation of molecular sieves with specific and improved functionalities, achieving novel materials with extraordinary and unique properties. The principal aim of the present paper is to highlight the major successes on the rational “one-pot” synthesis of functional zeolites, describing the benefits of the “direct route” methodology.
First, zeolites with well-distributed active sites, both metallic (metal-containing zeolites) and organic (hybrid organic-inorganic zeolites), synthesized by "one-pot" methodologies, are described. Second, direct synthesis of zeolites with large mesopore openings (hierarchical microporous-mesoporous materials) or with small particle size (nanosheets or nanozelites), both designed for minimization of diffusion problems, are also illustrated. Finally, new industrially relevant direct synthetic routes of zeolites in absence of organic structure directing agents (OSDA-free conditions) are shown.

2. Direct Synthesis of Functional Zeolitic Materials

2.1. Direct Synthesis of Metal-Containing Materials

2.1.1. Metals in Framework Positions. Zeolites are commonly synthesized and used in their aluminosilicate form [4]. The introduction of a trivalent atom, as aluminium, in tetrahedral coordination in the zeolite framework creates a negative network charge, which is compensated by a proton directly after calcination of the as-prepared zeolite, or after NH₄⁺ exchange and posterior calcination. These protons, allocated in the proximity of the aluminium atoms in framework positions, introduce strong Brønsted acid sites that can be catalytically used in numerous acid catalyzed chemical processes [1, 4].

Aluminosilicates are easily obtained by direct synthesis. Indeed, aluminosilicate zeolites can be found in nature, where those natural zeolites can crystallize in volcanic rocks by reaction with alkaline groundwater [5]. Natural zeolites show low Si/Al ratios due to the presence of large amount of extra-framework alkaline cations (as Na⁺, K⁺, or Ca²⁺).

The first synthetic zeolites obtained in the laboratory presented similar low Si/Al ratios due to the fact that they were hydrothermally synthesized in the presence of small inorganic cations [6, 7]. In 1961, Barrer and Denny introduced organic cations in the synthesis media for the first time, establishing the organic structure directing agent (OSDA) concept. The use of tetraalkylammonium cations allowed the preparation of high-silica materials (low aluminium content) with extraordinary hydrothermal stability and acid properties, being the first important breakthrough for the industrial application of acid zeolites [8]. Since this early introduction of organic molecules in the preparative gel, many types of organic molecules have been studied as OSDA in aluminosilicate synthesis. Indeed, structural characteristics of the zeolite, such as pore and cavity dimensions, depend on the shape, size, and hydrophobicity of the OSDA molecule [9–11]. The use of OSDA in combination with small inorganic structure directing agents has allowed the direct synthesis of innumerable zeolites in the aluminosilicate form. In the present review, I would like to give a general vision of the "state of the art" of the direct synthesis of functional zeolites, a full revision of aluminosilicates ever described, where beta is formed by a three-dimensional large pore system (openings of 6.5–7 Å) [16], and ZSM-5 is formed by a three-dimensional medium pore system (openings of 5–5.5 Å) [17].

Zeolites with well-distributed active sites, both metallic and organic, have been synthesized by "one-pot" methodologies, are described. Second, direct synthesis of zeolites with large mesopore openings (hierarchical microporous-mesoporous materials) or with small particle size (nanosheets or nanozelites), both designed for minimization of diffusion problems, are also illustrated. Finally, new industrially relevant direct synthetic routes of zeolites in absence of organic structure directing agents (OSDA-free conditions) are shown.

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On the other hand, the insertion of transition metals other than Al in zeolite framework may lead to unique catalytic properties. The main advantage of inserting transition elements by direct synthesis is related to the possibility of achieving a high dispersion of the metal in the zeolitic structure. However, the introduction of a metal in framework positions is complicated and will depend on the synthesis conditions, such as presence of cations, pH, and source of metal used, among others. The isomorphic substitution of Ti atoms into the zeolite framework is one of the most important findings in zeolite synthesis. The first titanosilicate molecular sieve described was Ti-silicalite (TS-1) by Eni researchers [18]. TS-1 is isosstructural to ZSM-5, and has been applied as catalyst in different oxidation reactions, such as aromatic hydroxylation and epoxidation of alkenes [19]. However, TS-1 zeolite showed diffusion restrictions when large molecules were reacted, requiring other titanosilicates with larger pores. The preparation of large pore titanosilicate beta zeolite (Ti-beta) allowed reacting bulky molecules in oxidation reactions with good activity and selectivities to desired oxidized products [20]. Both titanosilicate molecular sieves were prepared by direct synthesis methodologies, introducing Si and Ti sources in the preparative synthesis gel. Other medium and large pore titanosilicates have been synthesized by direct procedures [21, 22]. Nevertheless, some important titanosilicates, such as Ti-MWW related structures, which show the highest activity and selectivity for olefin epoxidations reactions, are only synthesized by rationalized post-synthetic procedures [23, 24]. Their preparation requires the presence of boron atoms acting as supporting structure directing agents, and later, those atoms are selectively removed by acid treatments, and replaced by titanium atoms [23, 24]. Those are clear examples illustrating that the direct synthesis of metal-containing zeolites is not always feasible, and the adequate synthesis conditions have to be found to favor the "one-pot" incorporation of the metal in framework positions.

The direct incorporation of tin in tetrahedral coordination into the zeolite framework of beta has resulted in very active catalysts with isolated single Lewis acid active sites for Baeyer-Villiger and Meerwein-Ponndorf-Verley reactions [25, 26]. Due to the higher atomic radius of Sn when compared to Si, the amount of Sn in tetrahedral coordination incorporated in the crystalline framework is limited, and theoretical studies have revealed that isolated Sn in the framework is partially hydrolyzed [27]. However, Sn-beta material has recently attracted much attention because it performs extremely well as heterogeneous catalyst in biomass-derived transformations, as the synthesis of lactic acid derivatives [28], and sugar isomerizations [29–31]. In addition to Sn-beta, very few stannosilicates containing tin in tetrahedral coordination have been obtained by direct synthesis methodologies (MFI, MTW, and MEL) [32–34].
Other direct syntheses of metal-containing zeolites in framework positions include iron [35, 36], vanadium [37–39], gallium [40], or cobalt [41–43].

In the 80s, researchers from Union Carbide described a new family of microporous molecular sieves, called aluminophosphates (AlPOs), whose composition comprised alternated P and Al atoms in tetrahedral coordination, connected by O atoms [44]. Interestingly, P and Al can be easily substituted by Si atoms or other metals (such as for example Mg, Mn, Zn, Co, Ti, V), directing the formation of silicoaluminophosphates (SAPOs) or metalloaluminophosphates (MeAlPOs), respectively [45]. Since the discovery of SAPOs and MeAlPOs, numerous reports dealing with the direct synthesis of those materials have appeared in the literature. This research was motivated by the higher levels of metal substitution achieved in AlPOs than in zeolites, allowing higher amounts of isolated metal atoms within molecular sieve frameworks with excellent acid and redox catalytic properties [45].

Among the all described silicoaluminophosphates, SAPO-34 molecular sieve is particularly interesting. This material is a small pore molecular sieve with large cavities in its structure, being extensively studied in several catalytic applications thanks to its particular structure and medium acid-strength [46]. SAPO-34 is an excellent catalyst for methanol-to-olefins (MTO) reaction, yielding large amounts of both ethylene and propylene with low formation of heavier products [46]. Indeed, UOP and Norsk Hydro first commercialized the use of SAPO-34 for MTO [47].

Several metalloaluminophosphates have also been directly synthesized since the very first description reported by Union Carbide researchers [48]. A large list of metals, including Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, have been introduced in the framework of more than 25 different metalloaluminophosphate structures with very diverse framework topologies [49]. Those materials are used as acid or redox catalysts [49]. Especially remarkable is their application as redox catalysts, due to tetrahedral isolated metal atoms into the molecular sieve framework which can undergo changes in their oxidation state. For example, Thomas et al. reported the selective oxidation of linear paraffins over Co- and Mn-containing MeAlPOs, observing remarkable regioselectivities towards oxyfunctionalized products at the terminal carbon atom [50, 51].

2.1.2. Metals in Extra-Framework Positions. Traditionally, the introduction of cationic metals or metal clusters in large or extra-large pore zeolites is performed by cationic exchange [52, 53], impregnation [54], or chemical vapor deposition [55, 56] of metal precursors after zeolite crystallization. However, these post-synthetic procedures have important drawbacks, such as the need of several steps to achieve the required metal-containing zeolite, the lack of uniformity in the distribution of the metal within the channels and cavities, and the limitation for efficient diffusion of the metal in small pore zeolites depending on its ionic radius.

The direct synthesis of metal-containing zeolites in extraframework positions would avoid the multi-step methodology, reducing considerably the economy of the process, and making this methodology very attractive for the industry. However, this direct methodology is not an easy task, since each metal-zeolite preparation has to be individually rationalized because success in the incorporation of a specific metal into a specific zeolitic framework will depend on the zeolite synthesis conditions, the metal precursor, and the metal-stability under those conditions. Next, some of the most interesting achievements in the last years will be presented.

RuO2-based nanoparticles catalysts have been presented as excellent catalysts in selective oxidations, as, for example, the oxidation of CO with oxygen below room temperature [57–59]. In general, the catalytic properties of supported-metal materials are defined by the nanoparticle size and shape. Indeed, the design of solids where the size of metallic particles remains stable during catalytic tests is a significant challenge. Interestingly, Zhan et al. [60] and Altwasser et al. [61] have reported the direct synthesis of entrapped RuO2 nanoparticles confined within the void volume of large pore and medium pore zeolites, respectively. On one hand, Zhan et al. synthesized RuO2 nanoclusters in the supercages of FAU zeolite by one-step hydrothermal method [60]. The supercages of FAU zeolite defined the RuO2 nanoparticles, resulting in 1.3 nm in size. This novel metal-zeolitic composite performed the aerobic oxidation
of alcohols under mild conditions with high activity and selectivity, and most importantly, the catalyst is both stable and reusable thanks to the RuO$_2$-entrapping within FAU cavities. In a similar way, Weitkamp et al. have directly synthesized RuO$_2$-entrapped nanoparticles in the MFI zeolite [61]. Those metal nanoparticles ranged between 0.5 and 0.9 nm in diameter, and were primarily located inside the pores of the MFI zeolite. The competitive hydrogenation of 1-hexene and 2,4,4-trimethyl-1-pentene was used as catalytic test to demonstrate the unique shape-selectivity properties of this RuO$_2$-entrapped MFI.

The direct synthesis of RuO$_2$-based zeolitic catalyst has been extended to small pore zeolite LTA [62]. As described above, the encapsulation of metal clusters in small pore zeolites is especially challenging, because the small pore size impedes using post-synthetic methodologies (wet impregnation, cation exchange, or chemical vapor deposition). Iglesia et al. reported the direct encapsulation of RuO$_2$ nanoclusters with 1 nm of diameter within LTA cages [62]. This RuO$_2$-LTA catalyst not only showed high activity in the hydrogenation of ethene, but also high resistance of the Ru clusters against poisons, as organosulfur compounds.

Encouraged by the excellent results obtained after encapsulating RuO$_2$ nanoclusters in small pore LTA zeolite, Choi et al. rationalized a general strategy to entrap different metal clusters within small pore zeolites by direct hydrothermal crystallization [63]. For this purpose, metal clusters were stabilized against hydroxide precipitation in the synthesis media by using bifunctional (3-mercaptopropyl)trimethoxysilane ligands (see Figure 2). On one hand, the mercapto group interacts with the metal, and on the other hand, the alkoxysilane group allows the incorporation of the metal-sulfur complex into the zeolite during crystallization process. This methodology allowed the incorporation of Pt, Pd, Ir, Rh, and Ag clusters with controlled sizes (1 nm) within LTA zeolite. These materials were very active in the hydrogenation of ethene and isobutene, and interestingly, the confinement of the metal clusters in the LTA cavities protected them against thermal sintering and also against deactivation by presence of organosulfur species.

The direct use of organometallic complexes as organic structure directing agents in the synthesis of molecular sieves has resulted in a very interesting methodology to achieve metal cations in the cavities of small-pore microporous materials. The pioneering works by Wright et al. allowed the direct preparation of Ni-containing aluminophosphates based on the use of nickel complexes, as for example Ni-complexes for the preparation of Ni-based molecular sieves, both containing small pores with large cavities, were synthesized using Ni-tmtact complex as template. Ni cations remained in zeolitic cavities after calcination, being balanced by negative charges present in the inorganic framework. Wright et al. also reported other Ni-complexes for the preparation of Ni-based molecular sieves, using both linear and macrocyclic polyamines [65, 66]. In this sense, several Ni-containing aluminophosphates, as CHA, AFI, AEL, SAS, or SAV, have been prepared with Ni-complexes, showing excellent catalytic properties in butane transformation to methane [65]. Among the Ni-complexes, the use of linear polyamines (diethylenetriamine and dipropylenetriamine) is of special interest because they are much cheaper than macrocyclic polyamines. Consequently, their implementation as templates in the direct synthesis of metal-zeolites results in inexpensive materials, which are attractive for industry.

Following this low-cost metal-amine complexes principle, Ren et al. have recently reported the direct synthesis of small pore Cu-SSZ-13 zeolite using Cu-tetraethylenepentamine (Cu-TEPA, see Figure 3) as the only template [67]. This Cu-TEPA complex shows the adequate geometry to template the CHA cavity of SSZ-13, obtaining extra-framework cationic Cu$^{2+}$ species after calcination within CHA cages. These type of metal sites, especially Cu$^{2+}$ situated close to the double-6-rings (D6R) present in CHA cages, have been described as active sites for the selective catalytic reduction (SCR) of NOx [68]. Indeed, directly synthesized Cu-SSZ-13 material showed good catalytic performance in the NH$_3$-SCR reaction [67].

However, Cu-SSZ-13 described by Xiao et al. shows some drawbacks, such as low Si/Al ratio (ranged between 4.1 and 7.5) resulting in low hydrothermal stability, and the Cu-loading cannot be easily controlled (Cu/Si ratio ranged between 0.09 and 0.10) [67]. A rationalized direct method overcoming those problems has been very recently described by Martinez-Franco et al. [69] The authors reported the direct preparation of the silicoaluminophosphate form of CHA structure, SAPO-34, containing Cu atoms in extra-framework positions by combining the use of a Cu-complex (Cu-TEPA) with a cooperative small organic molecule (diethylenamine) acting as cotemplate. By using this cooperative method, the Cu-loading into the molecular sieve was controlled, achieving also extraordinary solid yields. More importantly, synthesized Cu-SAPO-34 samples were extremely active and hydrothermally stable in the SCR of NOx reaction under very severe reaction conditions, presenting an opportunity for their industrial application. A similar direct cooperative approach has been reported by Deka et al. for the synthesis of Cu-SAPO-34, obtaining also excellent activities in the NOx-SCR reaction [70].

Other example of “one-pot” synthesis of Cu-containing small pore zeolite by the cotemplateing route is the Cu-STA-7 preparation [71]. In this case, copper cyclam and tetraethylammonium cations were used as cotelplates for the direct synthesis of Cu-STA-7 molecular sieve. Cationic Cu$^{2+}$ species within STA-7 cavities allowed good activities in the NOx-SCR reaction even in presence of water vapor, demonstrating that Cu-STA-7 material was hydrothermally stable under severe conditions.


The introduction of organic moieties within the pores or in the framework of microporous molecular sieves would allow tailoring the physicochemical properties of these inorganic materials, broadening their shape-selectivity properties due to the different nature of the organic functional groups. In this sense, functional organic groups attached to the zeolite
walls can offer different adsorption capacities to the hybrid zeolite when hydrophobic organic groups are inserted, or can offer unique catalytic properties depending on their acid/base character.

The adequate synthesis methodology to obtain organic groups uniformly distributed within the microporous crystals involve a direct synthesis, as organic groups introduced by post-synthetic methods (i.e. grafting) tend to attach to the external surface of the material rather than inside the pores [72].

The first microporous inorganic-organic polymers reported were zirconium-phosphite-diphosphonate materials, formed by zirconium phosphate layers pillared by organic groups [73–75]. However, the first description of full three-dimensional inorganic framework containing organic groups was described by Maeda et al. [76]. The authors described the direct hydrothermal synthesis of the AlMepO-β material, which is an aluminophosphate (AlPO) material with methyl groups in its structure. As presented above, AlPOs were described by Union Carbide researchers in 1982 [44], and they are formed by Al and P atoms in tetrahedral coordination interconnected by O atoms, leading to three-dimensional microporous materials [77, 78]. Maeda et al. used methylphosphonic acid as P source to introduce the organic modification, yielding the methyl-modified AlPO after the hydrothermal treatment. The structure of this novel hybrid organic-inorganic molecular sieve is very interesting, since it contains a unidimensional extra-large 18-ring channel (see Figure 4(a)) [79]. The size and shape of micropores can be modified by changing the organic group of the former phosphonic acid and the synthesis conditions.

The same authors reported the synthesis of a related methyl-substituted AlPO, AlMepO-α [81]. This material was also synthesized using methylphosphonic acid as P source, but at different hydrothermal conditions. Similarly to AlMepO-β, the inorganic framework of AlMepO-α is also formed by unidimensional extra-large 18-rings channels with all of the methyl groups pointing toward the center of those channels (see Figure 4(b)), creating pore openings close to 7 Å, as determined experimentally. Interestingly, Carter et al. have shown empirically and by theoretical calculations that AlMepO-α material is thermodynamically more stable than AlMepO-β [80]. Those two materials show high hydrophobic character because of the presence of methyl groups in the channels [76], and consequently, they show unique gas and vapour adsorption properties [82–84].

A remarkable achievement was the synthesis of hybrid silicoaluminates containing small organic groups in the zeolite framework reported by Yamamoto et al. [85]. They
prepared different zeolitic phases, as MFI and LTA, containing methylene-bridged organo-groups (Si–CH₂–Si) that replaced some siloxane bonds (Si–O–Si). For their preparation, bis(triethoxysilyl)methane molecules were introduced in the synthesis media together with the other gel components, and the resulting gels were autoclaved at high temperatures to achieve the crystalline organo-zeolites (see Figure 5). The presence of the C-Si bonds was clearly demonstrated by ²⁹Si and ¹³C MAS solid NMR. The organo-modified LTA zeolite showed larger n-hexane adsorption capacity than regular LTA zeolite. The same authors reported the preparation of other organo-modified zeolitic materials, ZOL family [86, 87].

Diaz et al. [88] and Su et al. [89] have described the synthesis and characterization of new hybrid organo-zeolites containing high organic content following a similar synthesis methodology to Yamamoto. On one hand, Diaz et al. [88] used bridged organosiloxane precursors as silica sources, containing methylene and ethylene groups. They achieved the hybrid ITQ-21, MFI, and BEA materials with the highest carbon content ever reported (∼9 wt%). The presence of the organic groups was confirmed by ¹³C and ²⁹Si MAS NMR and IR spectroscopy. On the other hand, Su et al. [89] described the preparation of the methylene-modified X zeolite, using bis(triethoxysilyl)methane as the only silicon source. This hybrid zeolite showed an extraordinary hydrophobic nature, as revealed by thermogravimetry.

Other methods using bridged organosiloxane precursors have been reported by different authors for the synthesis of hybrid aluminophosphate molecular sieves. Maeda et al. tailored two different pore-sized molecular sieves, as AFI (large pores) and VPI (extra-large pores) with diverse organic groups, as methyl, phenyl or methylene [90]. The hydrophobicity and acidity of those hybrid molecular sieves
were modified by controlling the amount and type of organic groups attached. Zhoe et al. also described the organic modification of large pore alumiophosphates AFI and AEL, by introducing 1,4-bis(triethoxysilyl)benzene in the synthesis media [91].

Very recently, ENI researchers have shown a new family of hybrid organic-inorganic crystalline phases referred as ECS (Eni Carbon Silicate) [92]. These materials were synthesized in alkaline media using different triethoxysilanes (benzene, biphenyl, ethyl-benzene, and propane) as silica sources. Interestingly, diverse organozeolite topologies were achieved, depending on the organo-substituted silane and synthesis conditions. The most remarkable examples are ECS-2 [92], ECS-3 [93], and ECS-14 [94]. ECS-2 is a clathrasil-like material with a regular stacking of aluminosilicate and phenylene, forming large cavities disconnected from the exterior. ECS-3 is a crystalline microporous material containing also phenylene groups in its structure, which is composed by two crystallographic independent small pores (8-rings, see Figure 6(a)) [93]. Finally, ECS-14 is a crystalline hybrid aluminosilicate synthesized using triethoxysilyl-benzene as silica source, and its structure is very similar to regular AFI aluminophosphate with linear large pores (12-ring openings, see Figure 6(b)) [94]. Not only ECS-14 organo-zeolite show excellent catalytic properties for the Claisen-Schmidt condensation of benzaldehyde and acetophenone, but also extraordinary optical properties with application in antenna systems were described [94].

Davis et al. have shown an interesting methodology to prepare new organic-functionalized molecular sieves showing shape-selectivity when used as catalysts [95]. The direct synthesis of different zeolites containing phenethyl groups in the gel allowed well intracrystalline dispersion of the organic groups tethered to the framework. The sulphonation of those phenyl rings introduced sulphonic acid sites that performed as shape selective acid catalysts. The authors illustrated this exceptional catalytic behavior reacting different sized organic molecules, as cyclohexanone and 1-pyrenecarboxaldehyde. Other organic functionalities, such as amine or thiol, have been also reported [96–98].

A very novel concept using monomers required in the preparation of conducting polymers as organic structure directing agents (OSDA) for the synthesis of microporous molecular sieves has been described by Corma et al. [99]. A precursor of poly-para-phenylenevinylene (PPV), as para-phenylenemethylene, was used as OSDA in the synthesis of microporous materials. These directly synthesized hybrid composites were transformed to PPV-entrapped inside the inorganic matrix. The resultant material showed excellent electrical conductivity and electroluminescence, while avoiding the degradation of the conducting polymer by oxidative degradation of the π conjugation.

2.3. Direct Preparation of Hierarchical Zeolites. Zeolites are widely employed as catalysts because of their unique structure [3, 4]. However, the restricted pore size (<1 nm) may induce some diffusion problems when bulky reactants or products are used in specific catalytic applications, especially those related to the oil upgrade and synthesis of fine chemicals [100]. The application of mesoporous materials, which show pore openings higher than 2 nm, in some of these processes has not succeed owing to their low hydrothermal stability [101]. Therefore, the pore accessibility of zeolites has to be improved by synthesizing well-structured microporous materials with larger pores [102, 103], or by creating secondary mesoporous systems within the microporous zeolitic matrix [104, 105]. The preparation of hierarchical materials containing micro- and mesoporosity is the preferred alternative.

Different approaches can be followed to create the mesoporosity in the zeolite crystals [106]. The most general choice is based on post-synthetic modifications, called destructive strategies [105], because of their simplicity. In these destructive strategies, the mesoporosity is created by the selective extraction of atoms, mostly Si or Al, from the zeolite framework.Dealumination or desilication post-synthetic procedures are based on calcination, steaming, acid leaching, or chemical treatments [105]. However, very important advances have been achieved in the direct or “one-pot”
synthesis of hierarchical structures. These rationalized preparations allow reducing the number of synthetic steps for the preparation of micro-meso silicates, and would introduce interesting industrial applications if the used mesoporous-templates were inexpensive or could be recycled [107].

The double templating route to synthesize hierarchical zeolites has been extensively described in the literature. In this method, mixture of two distinctive templates, directing microporosity or mesoporosity respectively, is introduced in the synthesis media. The mesoporosity can be induced by soft or hard templates. The main difference between those two types of mesoporous-directing agents is that soft templates are long surfactant chains, while hard templates are solids [108].

2.3.1. Direct Synthesis of Hierarchical Zeolites by Dual Templating with Soft Templates. One of the first attempts to prepare a mesoporous zeolite with high microporosity and acidity using a mixture of an alkyltrimethylammonium and a surfactant was reported by Karlsson et al. [109]. They hypothesized that the alkylammonium cation could direct the crystallization of the zeolite whereas the surfactant could simultaneously direct the formation of the mesopores by micellation. However, physical mixtures of microporous molecular sieves and amorphous mesoporous material were observed.

Despite this methodology could be very susceptible to achieve mixtures of materials, in recent years several descriptions have appeared in the literature claiming pure hierarchical structures by combining molecular and supramolecular templates.

Sakthivel et al. illustrated the one-step synthesis of a highly stable mesoporous molecular sieve with a structure similar to MCM-48 but containing zeolitic building units [110]. They used tetrapropylammonium (TPA) cation for the formation of the zeolitic framework, and a micellar solution of the surfactant cetyltrimethylammonium (CTMA) for the formation of mesopores. In a similar way, Chen et al. described the synthesis of a mesoporous ZSM-5 using one-step synthesis with dual templates. Mesopores were created by CTMA, and the crystalline wall of ZSM-5 by TPA. Polyethylene glycol (PEG), with an important role in the preservation of the mesoporous, and ammonium fluoride were also introduced in the synthesis media. The synthesized hierarchical structure showed extremely high hydrothermal stability [111]. Zhou et al. used conventional block copolymers (e.g., F127, or P123) as soft templates for the direct synthesis of mesoporous zeolites [112]. The main difference with the previous descriptions was that the synthesis gel was dried, and then, the crystallization was performed by steam-assistance. Under those conditions, block copolymer acts as a scaffold keeping the confined space during gel transformation. This hierarchical material showed enhanced catalytic activity in cracking and esterification reactions. Zhu et al. have also described the synthesis of hierarchical mesoporous zeolites by kinetic control on the zeolite seed formation [113]. They first aged the gel containing the zeolitic precursors at low temperature, favoring the formation of zeolite subnanocrystals, and later, soft template CTMA was introduced in the medium (see Figure 7), and the resulting gel heated at 150°C. The mesoporous ZSM-5 showed higher catalytic activity than microporous zeolites for the condensation of large molecules.

Very recent examples following the dual soft templating methodology by combining TPA and a surfactant molecule as cooperative templates have been reported for the direct synthesis of mesoporous titanosilicate TS-1. Vernimmen et al. described a facile one-pot synthesis of a trimodal siliceous material with controllable mesoporosity and microporosity, in combination with uniform macroporous
MFI or mesoporous MCM-41 [116]. The retardation of catalytic redox properties, reducing diffusion problems thanks to the meso- and macrohopes. Wang et al. have presented the one-pot synthesis of mesoporous TS-1 microspheres [115]. A triblock copolymer (F127 or P123) was used as surfactant, achieving TS-1 nanoparticles of 50–100 nm assembled into microspheres with regular intercrystal mesopores of 6–10 nm. Mesoporous TS-1 microspheres showed high activity in the oxidation of bulky molecules such as 3-picoline or cyclohexene.

In 2006, Choi et al. illustrated a new concept in the preparation of hierarchical zeolites by introducing rationalized amphiphilic organosilane surfactants to the synthesis gel (see Figure 8) [116]. Following this methodology, the phase separation phenomenon observed with ordinary surfactants is avoided, since silane groups facilitate the interaction of the functional surfactant with the growing zeolite crystals. In this sense, the amphiphilic molecule shows three clearly differentiated functional fragments, a hydrolysable methoxysilyl group, a quaternary ammonium acting as OSDA, and a hydrophobic alkyl chain (see Figure 8). Different mesoporous zeolites with uniform mesopore diameters were prepared by this method, but most interestingly, the mesopore diameter on these crystalline materials could be easily tuned by changing the chain length of the organosilanes. This surfactant organosilane strategy has also been generalized for the preparation of mesoporous crystalline aluminophosphates, obtaining the mesoporous AlPO-5 and AlPO-11 with enhanced physicochemical properties [117].

Choi et al. have applied these new hierarchical zeolites as attractive catalysts in various industrially relevant chemical processes. The strong acidity showed by the mesoporous MFI zeolite, together with its large intracrystalline void volume, offered unique catalytic properties in reactions involving large molecules or avoiding catalyst deactivation by coke deposition. Indeed, the synthesis of jasminaldehyde, which is an important product in the fragrance industry, was clearly improved when mesoporous MFI was used instead of regular MFI or mesoporous MCM-41 [116]. The retardation of catalyst deactivation in different catalytic processes, such as isomerization of 1,2,4-trimethylbenzene, cumene cracking, or esterification of benzyl alcohol with hexanoic acid were also studied [120]. These reports are important in continuous flow processes, since the retardation of catalyst deactivation would offer cost-down effects. The catalytic improvement against deactivation of mesoporous MFI zeolite has also been studied for methanol-to-hydrocarbon (MTH) process [121]. The MTH catalytic lifetime of the hierarchical zeolite was increased more than three times if compared to the microporous MFI. The authors demonstrated that the coke formation was primary formed in the mesoporous pores, explaining the excellent behavior of mesoporous MFI against deactivation.

Other mesoporous zeolites synthesized by the amphiphilic organosilane surfactants were LTA [122], and FAU [123]. On one hand, a detailed synthetic work was performed to control the mesoporosity in the hierarchical LTA zeolite [122]. The mesopore size was tailored from 6 to 10 nm controlling the surfactant amount. As a new approach, pore diameters could be further expanded to 24 nm by adding triblock copolymers as co-pore-expanding agents. These mesoporous LTA zeolites showed excellent catalytic properties for the conversion of methanol to dimethyl ether and hydrocarbons, with enhanced product selectivities, catalytic activity, and lifetime. On the other hand, Inayat et al. have reported the synthesis of hierarchical FAU-type structure with unique threefold pore system by using a soft organosilane surfactant [123]. TEM images revealed the formation of zeolitic nanosheets in a house-of-cards-like assembly with mesopores of 7 nm. This hierarchical material shows large potential for their use as adsorbent or catalyst.

Interestingly, the hierarchical zeolites synthesized by using amphiphilic organosilane surfactants present mesopore walls covered with large quantities of silanol groups, being feasible the organic functionalization by post-synthetic grafting treatments. Organic functionalized hierarchical zeolites showed high hydrothermal stability and reusability in the Sonogasira coupling reaction [124].

Other authors have used similar approaches with bulky alkoxysilylated molecules to create mesoporosity in zeolite crystals. On one hand, Mukti et al. described the use of alkoxysilylated nonionic surfactants, as trialkoxysilylated alkyl poly(oxyethylene ether), for the preparation of hierarchical MFI crystals with narrow mesoporosity [125]. This novel non-ionic surfactant is low-cost, nontoxic, and biodegradable, offering interesting advantages for industrial applications. On the other hand, Serrano et al. introduced bulky silanes, as phenylaminopropyl-trimethoxysilane, as silylating agents. Their addition was done once the first zeolite entities were formed, with the aim to perturb the crystals growth [126]. The zeolite growth mechanism proposed by the authors was based on three clearly differentiated steps: first, formation of pseudocrystalline zeolite nuclei; second, anchoring of the silylating agent on external surface of the zeolite nuclei; and third, hydrothermal crystallization of the functionalized seeds, leading to hierarchical porosity. Using this silanized protozeolitic methodology, hierarchical TS-1 zeolite with remarkable catalytic activity in bulky olefin epoxidation reactions has been prepared [127, 128].
2.3.2. Direct Synthesis of Hierarchical Zeolites by Dual Templating with Hard Templates. A different dual templating method for creating mesoporosity in zeolites is based on the use of solid templates (so-called hard templates) in combination with traditional molecular templates. Various types of solids have been used as hard templates in the direct synthesis of hierarchical zeolites, such as carbon nanoparticles, carbon nanotubes, polymers, resins, or biological templates, among others.

Carbon has been exploited as an excellent and versatile hard template in the creation of mesoporosity in the zeolites by direct synthesis methodology. Haldor-Topsoe researchers were among the pioneers in the use of carbon-related templates. Their first report described the use of carbon nanoparticles (12 nm in size), where an excess of zeolite gel was introduced with the aim to induce the growth of the zeolite matrix around the carbon particles [119, 129]. Large zeolite single crystals of MFI encapsulating carbon nanoparticles were obtained, leading to the formation of large single crystals with a mesopore system by calcination (see Figure 9). Following this methodology, mesoporous titanosilicate TS-1 zeolite has been also synthesized [130].

The catalytic activity of mesoporous TS-1 in the epoxidation of linear and cyclic alkenes was compared with that of conventional TS-1. As reported, mesoporous TS-1 improved the catalytic activity of conventional TS-1 zeolite without changing the product selectivities. Similar synthetic pathway was followed by Xin et al. in the synthesis of mesoporous TS-1 zeolite [131]. Improved catalytic yields were obtained using this hierarchical TS-1 on phenol hydroxylation and methyl ethyl ketone ammoxidation using H2O2 as an oxidant.

The generation of mesoporosity by using carbon nanoparticles has been studied in the preparation of hierarchical silicoaluminate ZSM-12 [132]. Mesoporous ZSM-12 samples with different Si/Al ratios were synthesized, ranging from 40 to 100. Interestingly, Si/Al ratios in the mesoporous zeolites are similar to the Si/Al ratios in the synthesis gels, indicating that the carbon nanoparticles did not affect the crystallization efficiency of aluminium during the nucleation and crystallization. These hierarchical ZSM-12 materials were tested in the conversion of n-tridecane and 1,3-dimethylcyclohexane, observing an enhanced activity for the mesoporous ZSM-12 when compared to conventional ZSM-12 zeolites. Other mesoporous zeolites have been also reported, as MEL [133] and Y zeolite [134].

The synthesis of mesoporous zeolites using carbon nanoparticles as hard templates has been expanded to other zeolitic materials by incorporating fluoride anions in the synthesis media [135]. This achievement was important, since the synthesis conditions were broadened not only to alkaline media, but also to neutral or acid media. Then, different hierarchical zeolites (ZSM-5, ZSM-11, or beta), and also different mesoporous silicoaluminophosphate molecular sieves (SAPO-5 and SAPO-34) were prepared by the combination of the fluoride route with carbon-templating.

Haldor-Topsoe researchers have also reported the growth of mesoporous zeolite single crystals using multiwall carbon nanotubes (MWCN) as mesopore-directing agents [136]. The diameter of MWCN was 12 nm average with walls conformed by 6–8 graphene layers. In this case, mesoporous silicalite-1 was prepared directly by impregnation of carbon nanotubes by the synthesis gel, and the zeolite nucleation occurred in the void between the nanotubes. The final mesoporosity in the zeolite crystals was achieved by calcination at 600°C, thanks to the complete removal of MWCN. Transmission electron microscopy (TEM) images clearly showed the straight mesopores generated by the carbon nanotubes directing agents.

The same authors performed a very interesting exploration of mesopore templating with carbon during zeolite synthesis [137]. They used both carbon nanofibers and carbon nanoparticles as templates for creating cylindrical mesopores. Carbon nanofibers can be produced much cheaper than previously reported carbon nanotubes [138], reducing considerably the synthesis costs of hard-templated hierarchical zeolites. Depending on the carbon source and the synthesis conditions, the zeolite mesopore volumes, crystal sizes, uniformity of crystals, and tortuosity of mesopores...
template by carbon sources could be tuned. From this study, it was concluded that carbon nanofibers could be very promising secondary templates to achieve cylindrical mesopores with low tortuosity in zeolite crystals.

Other type of hard templates used as shape-directing mesoporosity in the direct preparation of mesoporous zeolites were anion exchange resins. As a representative example of this methodology, Toshova et al. introduced spherical beads of an ion exchange resin in the zeolite synthesis solution, achieving a silicalite-1/resin composite after the corresponding hydrothermal treatment [139]. The organic ion exchange resin was easily removed by calcination, yielding to hierarchical TS-1 microspheres.

Polymers have also been used as efficient hard templates in hierarchical zeolite synthesis. Kang et al. described the synthesis of microspheres of mesoporous zeolites created by direct self-assembly between the aluminosilicate precursor, the micropore template tetrapropylammonium, and poly-(methyl methacrylate) (PMMA) nanospheres [140]. PMMA nanospheres played a dual-functional role for the generation of both mesoporosity and spherical morphology. Following this synthetic route, mesoporous zeolite microspheres with different diameters (500 nm to 10 μm) were prepared. This is an important finding, since microspheres with porous structure are highly required in bioapplications [141, 142]. In a similar way, Holland et al. demonstrated the synthesis of macroporous silicalite by combining polystyrene spheres as hard templates with the use of an appropriate structure directing agent [143]. Bimodal pore ZSM-5 structure with macropores (250 nm average diameter) was reported.

Additionally to the artificial templates described above, natural complex templates with unique multilevel structures and morphologies can be used for the construction of hierarchically organized porous zeolites. These templates are inexpensive, abundant, and renewable. Dong et al. used wood, which is a natural composite of cellulose, hemicellulose and lignin, as hard template [144]. A seeded growth methodology was followed to create a hierarchical zeolitic tissue that mimics the initial cellular structure of wood. Valtchev et al. used other vegetal (Equisetum arvense) as biological hard template to create hierarchical molecular sieves [145]. The authors reported the in-situ zeolitization of the vegetal macrotemplate by the biogenic silica present in the fresh plant, as the Equisetum arvense contains 13% wt of silica. Thus, leaves of the plant were subjected to hydrothermal treatment in presence of precursor solutions, obtaining hierarchical MFI crystals. In a similar way, mesoporous beta zeolite crystals were also synthesized using Equisetum arvense leaves as hard template [146]. The presence of high silica content in the biotemplate allowed the control of both the macromorphology structure and the small crystal size of the nanoparticles.

2.3.3. Direct Synthesis of Hierarchical Zeolites by Individual Template in Combination with Inorganic Directing Agents.

Up to now, combinations of molecular microporous-pore creating agents with large, soft or hard templates for meso-macroporosity formation have been required in the direct synthesis of hierarchical zeolites. Moreover, all the above reported techniques yielded a non-regular pore distribution in hierarchical zeolites. Recently, thanks to the rational combination of organic and inorganic structure-directing agents in the direct synthesis of zeolites, the preparation of hierarchical molecular sieves with a unique channel system of mesopores structurally connected with regular micropores has been achieved [147, 148].

On one hand, ITQ-37 zeolite (see Figure 10(a)) was synthesized by using a bulky non-surfactant organic structure directing agent in combination with germanium atoms [59]. This exciting material not only showed pore size dimension approaching the mesoporous range, but also provided new insight towards targeting chiral crystalline frameworks with extra-large pores. On the other hand, ITQ-43 was synthesized following a similar synthetic approach to ITQ-37, achieving in this case a very open structure [60]. ITQ-43 structure is formed by cloverleaf-like channels with...
openings of 21.9 Å × 19.6 Å in the range of mesopores (see Figure 10(b)), interconnected by large pores of 6.8 Å × 6.1 Å.

2.4. “One-Pot” Synthesis of Zeolitic Nanosheets. As described previously, the restricted pore size (<1 nm) of zeolites may induce diffusion problems when bulky reactants or products are involved in the catalytic application. Other significant problems, often observed in oil-derived catalytic applications, is the catalyst deactivation by coke formation, which poisons the acid sites and/or blocks the pores of the zeolite [150]. Important improvements have been obtained with the design of hierarchical micro-mesoporous materials, as illustrated in the previous point of the present overview. However, in most of those hierarchical structures, the mesopore distribution along the crystals is not regular. The discovery of delaminated zeolites by exfoliating layered zeolite precursors was a tremendous breakthrough, due to the formation of ultrathin zeolites, such as ITQ-2 and ITQ-6, with thickness below 5 nm [151, 152]. These materials present a very high external surface area facilitating reactant accessibility to the catalytic active sites, and offering excellent catalytic opportunities not only in petroleum refining applications, but also in fine chemistry [153, 154]. However, these materials require several synthetic steps for achieving the ultrathin zeolite layers, such as synthesis of the layered zeolite precursor, layer swelling by surfactants, ultrasound-treatment for zeolite delamination, and calcination.

Recently, researchers from Korea have discovered a new synthetic route to directly synthesize single-unit-cell zeolite nanosheets [149]. The authors rationalized the zeolite nanosheets synthesis by designing a novel di-quaternary ammonium-type surfactant. As seen in Figure 11(a), the surfactant was formed by a long-chain alkyl group (C_{22}) and two quaternary ammonium groups spaced by a C_6 alkyl chain. The diammonium section allowed the crystallization of the zeolite sheets, while the long hydrophobic chain formed a micellar structure preventing the zeolite growth along the b-axis (see Figure 11(b)).

Using the bifunctional surfactant of Figure 11(a), 2 nm thick MFI nanosheets were synthesized with different Si/Al ratio in the final solids, and very large external surface areas (>700 m^2/g) [149]. These MFI nanosheets also showed excellent hydrothermal stability after steam-treatments at 700 °C. Interestingly, a deeper research on the structure directing effects of the multi-quaternary ammonium surfactant revealed that the multilayer thick conforming the zeolite nanocrystals could be tuned varying the number of quaternary ammonium groups in the bifunctional organic molecule [155]. In this sense, zeolites with three, five, or seven multilayers were obtaining when the surfactant enclosed two, three, or four ammonium groups, respectively (see Figure 12). Moreover, in a very recent paper, Jung et al. have described the synthesis of a MFI zeolite of 1.5 nm thickness by using the surfactant [C_{18}H_{37}−N^+ (CH_3)_2−C_6H_{12}−N^+(CH_3)_2−C_6 H_{12}−N^+(CH_3)_2−C_18H_{37}]−Br^−_3 as OSDA [156]. This thickness revealed that the monolayer is composed by only micropores, which means that it is thinner than a unit cell. The hydrothermal stability of these single-pore sheets was also comparable to that of a conventional zeolite.

As expected, those very thin zeolitic layers performed better than conventional MFI zeolites for the conversion of...
large organic molecules were tested, as for example in the synthesis of flavanone or bulky diacetals [149]. Moreover, MFI nanosheets deactivated more slowly than conventional MFI zeolite due to the lower coke deposition. The catalytic activity of silicoaluminate MFI nanosheets was also studied in other interesting industrial catalytic applications, such as gas-phase Beckmann rearrangement [157]. The conversion of cyclohexanone oxime to ε-caprolactam is a remarkable industrial reaction for the production of Nylon-6 [158]. This reaction is industrially performed by microporous MFI acid catalyst. Kim et al. have shown that MFI-nanosheet was a highly selective catalyst for this reaction, increasing catalyst lifetime by a factor of 10 as compared to the industrial bulk catalyst.

MFI nanosheets can be synthesized not only as silicoaluminates, but also as titanosilicates. Titanosilicate MFI with single-unit-cell thickness was synthesized recently by two research groups [160, 161], and both obtained similar results in the epoxidation of bulky olefins with H$_2$O$_2$ or r-butyl hydroperoxide as oxidants. They observed an improvement in the activity and selectivity towards desired epoxide products when MFI nanosheets were employed.

2.5. Direct Synthesis of Nanozeolites. In previous sections, hierarchical molecular sieves and zeolite nanosheets have been described as efficient catalysts in chemical processes when bulky molecules have to be reacted or high deactivation by coke deposition is present. In addition to those tailor-made materials, the synthesis of nanozeolites is an attractive alternative route for the achievement of microporous molecular sieves with reduced diffusion path lengths [162]. The decrease of the crystal sizes below 200 nm results in very high external surface areas, and additionally, active sites more accessible. The small size of the nanocrystals introduces unique properties, broadening the applicability of nanozeolites to other interesting fields, as optoelectronics, sensors, or biomedicine [163].

Nanozeolites can be prepared by confined-space methodology, which consists in a multistep synthesis procedure where a previously synthesized inert matrix, such a porous carbon or a polymer, provides the confined space for the nanozeolite growth [164, 165]. However, most of the synthetic procedures are based on the direct preparation from clear aqueous solutions and gels [162]. As a general approximation, the preparation of nanozeolites from clear solutions and gels requires synthesis conditions that favor nucleation processes against crystal growth. These conditions can be reached by using large amounts of organic structure directing agents in the synthesis gels to favor the supersaturation of zeolite nuclei, and low content of alkali cations to avoid the aggregation of the ultrasmall particles. Moreover, the introduction of enough alkali bases in the gel is a key factor, because the complete dissolution of silica and aluminium sources is absolutely necessary. The temperature of the synthesis is another important variable, since low temperatures favor nucleation processes and high temperatures favor the crystal growth [166].

Following the above described premises, several zeolite structures (FAU, LTA, SOD, ZSM-2, GIS, OFF, MOR, LTL, BEA, MFI, MEL, AFI, AEL) have been synthesized with sizes below 200 nm. Tosheva and Valtchev have nicely reviewed the preferred synthesis conditions used in the preparation of those nanozeolites [162]. Considering that the literature shows large number of papers dealing with the direct synthesis of nanozeolites, a selection of some illustrative achievements will be presented here, together with some attractive new applications for nanosized molecular sieves.

2.5.1. Examples of Nanozeolites Directly Synthesized from Clear Solutions or Gels. Beta zeolite is probably one of the most important zeolitic materials in industry. The preparation of nanocrystalline beta zeolite is a matter of great interest because the reduction of diffusion path lengths of bulky reactants and products can offer tremendous possibilities for its industrial application in several chemical processes.

The very first description of beta nanocrystalline was reported by Cambor et al. in 1997 [167]. Different synthesis parameters, the role of the alkali cations and the kinetics of crystallization were intensively studied [168]. A very nice correlation between the crystal size and the Si/Al ratio in the nanozeolite was observed (see Figure 13).
Similarly, Schoeman et al. synthesized nanocrystalline beta zeolite with less than 150 nm within a wide composition range [169]. In this study, nanosized beta was favored by low water and sodium ratios, and high TEAOH contents. The Si/Al ratio achieved was close to 23. Interestingly, these colloidal beta nanocrystals were used as seeding agents in the microporous films preparation. The same authors also described the direct synthesis of the pure silica form of nanozeolite beta at similar conditions [170].

Recently, UOP researchers have presented new direct synthetic routes for the synthesis of the beta nanoneolite [171, 172]. They observed a significant reduction in crystal size when temperature and water content were lowered, tetraethylorthosilicate was used instead of fume silica as raw material, the content of the structure directing agent was increased, and a surfactant was used in the synthesis medium [171]. In addition, the synthesis of nanosized beta zeolite with particle sizes of 140 nm was achieved by using 4,4’-trimethylenedioxy(N-methyl, N-benzyl-piperidinium) as structure directing agent [172].

High-silica ZSM-5 is the other most important zeolite in the industry. This material shows unique catalytic properties in numerous chemical processes, as methanol to gasoline (MTG) or several petrochemical processes. The size reduction of ZSM-5 crystals allows increasing the accessibility of bulky molecules to the active sites. The first description of the nanocrystalline ZSM-5 zeolite was reported by Persson et al. [173]. In this study, narrow size distributions of ZSM-5 zeolites were achieved in the range 130–230 nm. The preferred synthesis conditions required low sodium and high OSDA concentrations. Moreover, a decrease of the crystal size was observed for increasing aluminium contents, as observed in the synthesis of nanosized beta (see Figure 13).

Nanocrystalline ZSM-5 zeolite was also prepared by Van Grieken et al. following a similar procedure [174]. Very small crystal sizes, ranging from 10 to 100 nm, were obtained by hydrothermal synthesis of supersaturated homogeneous mixtures in absence of Na⁺ cations. Song et al. described the synthesis of nanocrystalline ZSM-5 using modifications of the clear solution procedures [175]. By varying the water content, ZSM-5 with uniform nanocrystals (~15 nm) and Si/Al ratios close to 20 were accomplished. Interestingly, those Si/Al ratios were the lowest values reported for nanocrystalline ZSM-5. Aguado et al. have synthesized ultrasmall ZSM-5 crystals at low temperatures (70–90 °C) and ambient pressures [176]. The resulting crystals not only ranged 10–20 nm, but also showed strong acidity, and high external surface.

All the nanocrystalline zeolite syntheses described above were carried out in aqueous medium. Those nanoneolites show hydrophilic external surface by the presence of large number of external silanols, which can limit the reactivity in some catalytic applications. However, a smart new methodology to synthesize uniform sized nanocrystallites with hydrophobic character was presented by Youn and Do et al. [177]. In this novel route, an organic solvent was used for the syntheses of nanosized zeolites instead of water, and zeolite precursors were functionalized with organic silane groups, becoming well dispersed in the organic medium. Moreover, the aggregation of crystals was prevented by the organic groups, yielding small and uniform 20 nm hydrophobic nanoneolites. Following this synthetic route, FAU nanoneolites with sizes ranging 25–100 nm were achieved using toluene and formamide as solvents. The same authors also described the preparation of nanoneolites in a two-phase (organic-aqueous) method, where smaller crystal sizes were achieved in the organic phase [178].

2.5.2. Applications of Nanozeolites. Nanozeolites have often been applied as efficient catalysts in chemical processes limited by diffusion. The decrease of the crystal size has benefits on activity and selectivity. For example, nanocrystalline zeolites have been used in catalytic cracking, reporting higher selectivities to gasoline and lower deactivation by coke when USY nanoneolite was tested [179]. The use of nanocrystalline beta zeolite allowed increasing the isomerization selectivity and sulfur resistance during the simultaneous hydroisomerization of n-heptane and hydrogenation of benzene [180]. The isomerization increase could be related to faster diffusion of the iso-C7 products, and the improved sulfur resistance to the better Pt dispersion on the high surface area. Nanocrystalline beta also showed excellent activities in the acylation of bulky 2-methoxynaphthalene [181].

Other major application of nanoneolites is their use in the preparation of supported zeolite films and membranes. For this purpose, nanocrystalline zeolites are adsorbed on a support, and then, induced to grow into a dense film by secondary growth. Many examples dealing with this topic can be found in literature [182, 183].

But more interestingly, zeolite nanocrystals have been introduced in new emerging applications, as for example sensing materials, low-k zeolite films, or biomedicine. As chemical sensors, nanoneolites have some attractive physicochemical properties, such as a greater uniformity of the pores for molecular discrimination, tunable hydrophobic/hydrophilic nature, and a high thermal and chemical
stability. Thus, new sensing devices based on nanocrystalline zeolites showed high selectivity to transform different molecules [184, 185]. Low-dielectric-constant (low-k) materials are required for building microprocessors, and they may present high mechanical, thermal and chemical stabilities. In recent years, low-k thin pure silica zeolitic films have been obtained by spin-coating silicalite-1 or beta nanozeolites [169, 186]. Several reports using nanocrystalline zeolites as novel materials with application in biomedicine have been recently reported. Gd-doped nanozeolites have been successfully used as magnetic resonance imaging (MRI) contrast agents [187, 188]. Biomolecules have been adsorbed and immobilized on nanozeolites thanks to their large external surface areas, making these materials attractive for drug-delivery systems [189, 190]. Also in vitro cytotoxicity studies of all-silica nanozeolites have been performed on different cell lines [191, 192].

2.6. Direct Synthesis of OSDA-Free Zeolites. The first examples of synthetic zeolites were prepared with Si/Al ratios close to 1, using alkali cations as the only templating cations [3]. Classical examples of low silica zeolites synthesized without organic molecules are X, Y, A, and L zeolites [193]. Tetraalkylammonium cations were introduced as organic structure directing agents (OSDA) in zeolite synthesis for the first time by Barrer et al. in 1961 [8]. Thanks to the OSDA incorporation into the zeolite, the Si/Al ratio in the framework increased. In the same way, the hydrothermal stability of the zeolites and the strength of their acid sites also increased, and consequently, the number of potential applications as catalysts. The rationalized introduction of OSDA, primary amines and quaternary ammonium cations, with different shapes and sizes has permitted the synthesis of large number of new amazing zeolitic structures [194]. However, the direct synthesis of high-silica zeolites in absence of OSDA, or OSDA-free conditions, is highly desired in the industry because usually the most expensive component in the molecular sieve synthesis is the organic template. In addition, the preparation of OSDA-free microporous materials would allow skipping the final calcination step required to remove the precluded organic moieties when a OSDA is used.

In the recent years, several zeolites with high Si/Al ratio have been reported for the first time in absence of OSDA molecules in the synthesis medium. In this sense, Xiao’s group at Jilin University has been one of the most active researchers in the rational preparation of OSDA-free zeolites. ECR-1 was the first zeolite reported by Song et al. in organic template free conditions [160]. ECR-1 is a large pore aluminosilicate formed by twin of mordenite-like sheets and mazzite-like cages. Traditionally, this material was prepared using organic templates, as bis(2-hydroxyethyl) dimethylammonium chloride [195], adamantamine diquaternary alkylammonium iodides [196], or tetramethylammonium cations [197]. OSDA-free ECR-1 zeolite was achieved by Xiao et al., by carefully adjusting the molar ratio of Na2O/SiO2 in the synthesis medium. The formation of ECR-1 framework subunits and zeolite crystallization were assembled by hydrated alkali metal cations. The SiO2/Al2O3 ratio in the final OSDA-free ECR-1 zeolite was 7.0, which is in agreement with the organic-templated ECR-1 [195].

A different approach introduced in the synthesis of new OSDA-free molecular sieves is based on seeding methodology. It was known that the addition of zeolite seeds in the synthesis gels containing organic templates allowed accelerating the crystallization rate of the desired zeolite, and several examples were reported in literature [198–200]. Following the seeding methodology, but now in OSDA-free medium, Xie et al. first described the organotemplate free fast synthesis of beta zeolite [201]. Traditionally, beta zeolite was prepared using tetraethylammonium cation as organic structure directing agent [16]. However, following the seeding methodology, by adding seeds of calcined beta in the preparative gel in absence of organic additives, the OSDA-free beta was synthesized. The presence of seeds directed both the growth of beta crystals, and increased the crystallization rate considerably. This is an important discovery due to beta zeolite is a three-dimensional large pore zeolite with tremendous impact in petrochemistry and fine chemistry fields. Then, manufacture costs of this material would be considerably reduced by its OSDA-free preparation. Xie et al. further studied and characterized the OSDA-free beta zeolite, in order to understand how the nucleation mechanism occurs [202]. XPS measurements showed that the Si/Al ratio in the beta crystals was not uniform, with higher values in the crystal core than on the crystal surface. This finding clearly evidences that the crystal growth occurs from the seeds added in the initial synthesis gel. Moreover, the catalytic activity of this OSDA-free beta zeolite was tested in the catalytic cracking of a real industrial feedstock (Fushum light vacuum gas oil), observing much higher activity for OSDA-free beta than regular beta and Y zeolite. In addition, OSDA-free beta produced the highest yield of LPG, and at the same time, the lowest yield of heavy oil [202].

In a similar way, ZSM-34 zeolite could be synthesized as OSDA-free molecular sieve using zeolite L seeds [203]. This material was previously synthesized with organic structure directing agents, as choline [204] or different diamines [205]. The structure of ZSM-34 material is formed by an intergrowth of offrette and erionite, and interestingly, is used as efficient catalyst for the methanol to olefins reaction [206]. The use of seeds of zeolite L was pivotal in the preparation of ZSM-34 in the absence of templates, because zeolite L contains the same cages (called CAN cages) than ZSM-34, and in this sense, those small secondary building units can be considered as the real crystallization seeding.

Recently, Zhang et al. have also reported two other zeolitic structures, ferrierite [209] and mordenite [210], in OSDA-free synthesis conditions. Ferrierite, which is an interesting acid catalyst for isomerization processes [211], possesses a two-dimensional pore system with interconnected 10-ring and 8-ring channels [211]. High-silica ferrierite, with Si/Al ratio close to 15, was first synthesized in OSDA-free conditions using CDO crystals as seeding [209]. Mordenite is an important catalyst in several petrochemical processes (such as hydrocracking, reforming, alkylation, among other),
and its structure is formed by the interconnection of large 12-ring and small 8-ring channels [212]. OSDA-free mordenite material was achieved by adding a solution of mordenite seeds, directing the formation of nano-rod assembled single crystals. Iron containing mordenite zeolite was also synthesized by OSDA-free conditions, with potential applicability in selective catalytic reduction of NOx or hydroxylation of benzene.

Itabashi et al. have also worked on the preparation of OSDA-free zeolites by using the seeding methodology. Interestingly, nucleation and crystallization mechanisms on OSDA-free conditions in the presence of zeolite seeds were studied in detail by these researchers. OSDA-free beta zeolite was first selected as the model case for the study [207]. From detailed characterization measurements, Okubo et al. proposed a mechanism based on different steps for the crystallization of OSDA-free beta material (see scheme in Figure 14). First, seed embedded gel, which initially is a hard paste (Figure 14(a)), turns into solid amorphous silicoaluminate and liquid phase (Figure 14(b)). In this step, seeds of beta are disaggregated and introduced in the amorphous silicoaluminate. Second, the crystal growth occurs when partially dissolved amorphous aluminosilicate contact with small-sized zeolite seeds (Figure 14(c)), which provide the surface for the crystal growth. And third, once the amorphous phase is completely dissolved, the crystal growth is finished (Figure 14(d)).

Based on the proposed crystal growth mechanism for OSDA-free zeolites, Itabashi et al. extended their work to the synthesis of other zeolites. Mordenite, ferrierite, ZSM-5, ZSM-11 and ZSM-12, were prepared by the seed-assistance methodology [213]. Interestingly, the authors noticed that the zeolites formed from seed-free gels and zeolites obtained from seed gels show common composite building units. Also, Okubo et al. have reported the OSDA-free synthesis of the so-called “Green MTW” zeolite [214]. This material was achieved by using OSDA-free MTW seeds in the synthesis gel, providing the basis for a complete environmentally-friendly process for the manufacture of MTW zeolite.

A very interesting breakthrough in the seed-assisted synthesis of molecular sieves in the absence of organic template was recently described by Yokoi et al. [215]. RTH is a two-dimensional small pore zeolite, which contains large cavities in its structure, suggesting that this structure could be adequate for its application in methanol to olefin reaction. This material was previously synthesized using a pentamethylpiperidine [216] or an azoniumbicyclo cation [217] as organic structure directing agents. Yokoi et al. not only achieved the direct synthesis of the aluminium RTH zeolite (named Al-TTZ-1) under organic free conditions, but also remarkable catalytic results were reported for this new material in the methanol to olefin reaction. The methanol conversion values were nearly 100%, with extraordinary selectivities to propylene.

Ng et al. have described a new concept based on the “capture” of the zeolite during its preparation without the presence of organic structure directing agents [208]. As seen in Figure 15, ultrasmall EMT crystals (6 to 15 nanometers) were obtained at very low temperature (30°C) from template-free colloidal precursors. Low-temperature and OSDA-free are two conditions that are highly demanded in zeolite synthesis, as they would reduce costs and save energy. These mild synthesis conditions used in the EMT preparation can be easily scaled up, offering excellent opportunities for its application in catalysis, adsorption, or gas separation.

3. Perspectives and Conclusions

As it has been described along the present review, direct synthesis of zeolites is a tremendous innovative field. Since the first synthetic zeolites achieved in the laboratory by Barrer in the 50s [6, 7], the scientific community has been able to rationalize and introduce numerous new concepts.
to the synthesis methodology that have resulted in novel zeolitic materials with unique physicochemical properties. More than 200 different molecular sieve structures have been discovered along these almost 60 years of zeolite synthesis history [218], most of them with different chemical compositions, crystal size, or hierarchical pore structures. Despite this long history, and the large number of zeolites discovered, the researchers are still doing extraordinary advances in designing new zeolitic materials with attractive properties from scientific and industrial standpoints. Last year, “Science” recognized the tailor-made synthesis of zeolites as one of the “Ten breakthroughs of 2011” [219]. Some of the works highlighted there comprised the direct synthesis of functional zeolites, as the direct synthesis of hierarchical nanoporous architectures by using dual functional templates [220], the direct preparation of a hierarchical micro-mesoporous zeolite combining organic and inorganic directing effects [148], and the direct OSDA-free synthesis of ultrasmall EMT zeolite by capturing methods [208]. These recent achievements are only some examples underlining the importance of rationalizing and introducing new ideas and concepts in the design of new functional zeolitic materials.

The direct synthesis of metal-containing, both in framework and extra-framework positions, of new zeolitic structures with isolated metals, or small-metallic clusters, is a fast growing area. This direct synthetic route offers extraordinary opportunities to control the location of the metallic active sites in the final solid, and at the same time, the number of steps required in the synthesis is clearly reduced, making the methodology very attractive for the industry. Recent applications of metal-zeolites in fine chemistry or biomass-derived processes introduce exciting challenges in the direct synthesis of new functional metal-zeolites.

The direct preparation of hybrid organic-inorganic zeolites permits a good organic dispersion within the zeolite crystals. The recent discoveries presented by Eni researchers on the design of new hybrid materials with novel applications in catalysis and antenna systems, have introduced fresh strength to the field, opening new opportunities in the near future.

The rational direct synthesis of new zeolitic materials showing low diffusion-path, both hierarchical microporous-mesoporous zeolites and ultrasmall particle size (nanosheets and nanozeolites), is also a very hot topic. The ability of reducing mass transfer limitations together with high active site accessibility increases the catalytic potential of zeolites. In this sense, the recent direct synthesis of zeolitic nanosheets with different pore topologies and chemical compositions should introduce unique selectivities in new catalytic applications.
Finally, the direct synthesis of zeolites without the presence of organic structure directing agents is especially interesting for industry. Generally, the organic molecules used as templates increase the overall cost of the synthetic procedure. Recent advances using the seeding methodology have allowed the preparation of different zeolitic materials used in the industry without organic templates. Definitely, OSDA-free synthesis is a very challenging area, and in the near future, extraordinary achievements will be surely presented.

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