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Account / Revue

Organising disordered matter: strategies for ordering the network of mesoporous materials

Joaquín Pérez-Pariente *, Isabel Díaz, Javier Agúndez

Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

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Abstract

Several synthesis strategies used to obtain hydrothermally stable and highly active catalysts based on ordered mesoporous materials are reviewed in this contribution. It is experimentally observed that the use of zeolite precursors as building blocks of the mesoporous network yields the most stable materials. However, the nature of the mesoporous framework of these solids remains still unknown, and basic understanding of the assembling process of zeolite precursors and surfactants has not yet been achieved. Some key features of the whole process are explored, and examples that illustrate its chemical and structural complexity are provided. *To cite this article: J. Pérez-Pariente et al., C. R. Chimie 8 (2005).*

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Résumé

Structurer la matière : des stratégies pour ordonner le réseau des matériaux mésoporeux. On passe en revue dans cet article des stratégies utilisées pour la synthèse de matériaux mésoporeux ordonnés, à haute stabilité hydrothermale et catalytiquement actifs. On montre que les matériaux mésoporeux les plus stables sont obtenus avec des précurseurs de zéolites. Pourtant, la nature du réseau mésoporeux ainsi que les mécanismes qui contrôlent l'assemblage des précurseurs de zéolites et des surfactants restent inconnus. Les auteurs examinent quelques aspects clés du processus de synthèse, dont la complexité chimique et structurale est mise en évidence par les exemples rapportés. *Pour citer cet article : J. Pérez-Pariente et al., C. R. Chimie 8 (2005).*

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Keywords: Ordered mesoporous materials; Zeolite precursors; Crystalline mesoporous materials

Mots clés : Matériaux mésoporeux ordonnés ; Précurseurs de zéolites ; Matériaux mésoporeux cristallins

* Corresponding author.

E-mail address: jperez@icp.csic.es (J. Pérez-Pariente).

1. Introduction

There is little doubt that the flourishing and ever-increasing variety of catalytic processes invented and put into practice by chemists' and engineers' ingenuity relies upon order. In this context, order means the specific arrangement of atoms and molecules in the space that is required for the catalytic event to take place. In its broader sense, this statement holds for both homogeneous and heterogeneous systems, although we will be concerned in this review with the latter. Basically, the ordered geometrical configuration of atoms and molecules of a solid catalyst conveys chemical information to the reacting molecules. This concept was formerly developed for metals and metal oxides surfaces [1], but latter on it also covered a different class of non-metallic crystalline catalysts, the zeolite materials. The arrangement of four-connected TO_4 tetrahedral entities (the T-atom, silicon, aluminium or phosphorous usually, is located in the centre of the tetrahedron) not only creates the well-known intracrystalline cavities so characteristic of zeolite crystals, but also provides a very narrow set of T–O distances and T–O–T bonds that identify every zeolite structure. Moreover, a close relationship has been found between these structural parameters and acidity in crystalline aluminosilicates [2,3].

The potential use of zeolite materials in catalysis, depends not only upon the acid strength and acidity spectra, but also on the access of reacting molecules into the complex system of cavities and channels so characteristic of these crystals. It is indeed possible to take advantages of the well-known shape selectivity effects that the pore aperture and the topology of voids impose to the course of the catalytic reaction. However, for many potentially useful chemical reactions size exclusion virtually operates, as the steric requirements of the reagents or products are beyond the pore size limits of the known structures. Different approaches, which do not need to be repeated here [4], have been developed along the years to overcome this limitation. Among them, one of the most promising was the use of clusters of surfactant molecules (micelles) as templates of inorganic porous networks containing mesopores ($d_p > 2.0$ nm) [5]. As the size of the micellar aggregates is currently above 2.0 nm, the expectation that, if they behaved like the web of discrete template molecules present inside the zeolite pores, then they would lead to ultra-large pore materials, was plenti-

fully fulfilled. The three basic different materials initially invented and forming part of the so called M41S family, MCM-41, MCM-48 and MCM-50 [5], were joined rapidly by a variety of new structures, encompassing different void geometry and cavities connection. The healthy growing of the number of new mesoporous topologies of these fascinating materials has no doubt been fed by an increasing mastery of the sol-gel chemistry in presence of surfactant agents.

The potential catalytic capabilities of the mesoporous family of materials is, needless to say, enormous, [6,7] and it is enhanced by the possibility of tailoring their pore size. The presence of mesoporosity certainly vanished the pore size barrier previously existing for the use of (organised) porous materials in catalysis, but before application can be envisaged their intrinsic acid properties should be close to those of zeolite materials, and these properties depend upon the framework ordering. It was soon realised that the behaviour of conventional mesoporous materials in acid catalysed reactions fell short of expectations, and a low acid strength of aluminium-containing ordered mesoporous catalysts was generally found. Several studies evidenced the absence of ordering in the inorganic tetrahedral framework [8], in such a way that it has been hypothesised, based upon what is known about zeolite chemistry, that the low acid strength and hence poor catalytic performance were both due to the quasi-amorphous nature of the framework, i.e. it is characterised by a broad distribution of T–O–T angles. Once this hypothesis was established, different synthesis strategies were launched in order to improve framework ordering in mesoporous materials. Most of these procedures involve the use of concepts well established in the hydrothermal crystallisation of zeolites, and will constitute the core of this work. However, it is worth mentioning here that mesoporous zeolites have also been synthesised by using carbon nanoparticles to generate mesoporosity [9]. Before proceeding further, it would be of some interest to notice that few attention has generally been paid to another characteristic that differentiate clearly a typical zeolite framework from that of a mesoporous structure: the presence of a much higher concentration of silanol groups in the latter. In other words, the tetrahedral network of a mesoporous material is highly interrupted, the average connectivity per tetrahedral atom being much lower than that of zeolites. Figures of $Q_3/(Q_4 + Q_3)$ ratios in the range 0.3–

0.5 are rather common, as confirmed by ^{29}Si MAS NMR studies, regardless the structure type [10]. The question of whether a hypothetical improvement of ordering is possible for such low-connected frameworks remains open, but we are inclined to think that success in this field would run side by side with strategies aiming to decrease simultaneously the defects (silanol groups) population.

Professor Davis has argued that the lack of crystallinity of ordered mesoporous materials may be the result of the correlation between the framework density and the minimum ring size for every T-atom [11]. Due to their large void fraction, ordered mesoporous materials should have a large number of three-membered rings, but such small rings would not be particularly stable in pure silica or silica–alumina compositions [12]. Beside this argument, the correlation does not hold for structures containing non-tetrahedral atoms, and it would be then questionable whether it applies to frameworks with an average connectivity lower than four.

2. Synthesis strategies

The synthesis strategies put into practice have grown in sophistication with time, but it is nevertheless possible to integrate them into three different groups, according to the basic concepts underlying the experimental design and other operational factors.

The first approach (A), consists basically in the concept of ‘functional independence’ of the zeolite and mesoporous structure directing agents (SDA), both molecules being simultaneously present in the synthesis gel. Prior synthesis work by using short-chain tetralkylammonium cations based upon this concept can be traced back to the synthesis of SAPO-37, which requires tetra-

methylammonium to template the formation of sodalite cages, whose assembly in the FAU topology is promoted by tetrapropylammonium (TPA) cations, that are located inside the supercavity [13,14]. A more recent example is the synthesis of all-silica MCM-22 from mixtures of hexamethylenimine and *N,N,N*-trimethyladamantanammonium [15]. It is then conceived that the surfactant micelles self-assemble in order to build the mesoporous framework, whereas the zeolite template, TPA in most cases, would be able to produce the ‘zeolitisation’ of the pore walls, i.e. the formation of T–O–T connectivities similar, for example, to those present in MFI topology. An overview of the results reported following this procedure, and collected in Table 1, shows that this approach leads always to mixtures of mesoporous solids and zeolite crystals. As an example, Professor Van Bekkum reported the formation of a composite material consisting of zeolite Y with overgrowth of MCM-41 from a conventional MCM-41 synthesis gel containing relatively large amounts of sodium hydroxide and alumina [16]. A variation of this method consists of two-steps; in the first one the synthesis gel contains only the surfactant, while the zeolite template is added in the second step. Mixtures of MCM-41 and ZSM-5 are obtained following this procedure [17], Table 1. It has not yet been clearly demonstrated that these mixtures of phases offer more possibilities in catalysis than physical mixtures of both would.

In the second procedure (B), the mesoporous material synthesised in a first step is treated with a solution containing the zeolite template, aiming in this way to recrystallise the mesoporous framework. Kloetstra et al. [18] exchanged calcined MCM-41 (Si/Al = 30) with TPA, which is then heated at 120 °C in a glycerol solution. HMS (a mesoporous material synthesised by using long-chain primary amines [24]) was subjected to the

Table 1
Strategies for the synthesis of mesoporous materials with ordered walls

References	Route	SDA	Surfactant	Resulting materials
[17,20,21]	A	C ₆ TMAB	C ₁₄ TMAB	Mixtures of MFI and MCM-41 phases
[22]	A	TPAOH	CTAB	Composites ZSM-5-disordered mesoporous
[23]	A	TEAOH	CTAB	Mixtures of BEA and MCM-41 phases
[28]	A	TPAOH	CTAB	Ti-microporous mesoporous composite
[18,25]	B	TPAOH	CTAB	Mixtures of MFI and MCM-41 phases
[19]	B	TEAOH	CTAB	Full Si–Ti–BEA from Si–Ti–MCM-41
[26]	B	TPAOH	P123	ZSM-5 and disordered mesoporous phases
[27]	B	TPAOH	P123	TS-1 and disordered mesoporous or SBA-15
[29]	B	TPAOH	Chitosan	Mixtures of ZSM-5 and amorphous aluminosilicate

same treatment. The authors reported an increase of the catalytic activity of the treated materials compared to that of the parent ones, and observed an increase of the 550 cm^{-1} band in the infrared spectrum, usually assigned to vibrations of the five-membered ring present in ZSM-5. No XRD reflections characteristic of ZSM-5 were observed. It was later reported that the mesoporous structures collapse if the treatment is performed in water [22]. The authors claimed the formation of embryonic ZSM-5 structures. On the other hand, the treatment of MCM-41 impregnated with TPA under basic conditions leads to its partial transformation into 3 nm particles of ZSM-5 [25]. The hydrothermal treatment of a mesoporous material synthesised by using the tri-block copolymer (PE)(PO)(PE) surfactant Pluronic P123 with a TPAOH solution leads to mixtures of mesoporous/ZSM-5 [26], whereas the use of tetraethylammonium hydroxide (TEAOH) promotes the formation of a mixture of the starting material and zeolite Beta [23]. These results evidence that the mesoporous solid acts basically as a source of silicon and aluminium [19], even titanium [27,28], for the crystallisation of the zeolite material.

Procedure (C) is a two-steps process, aimed to mimic the physicochemical conditions prevalent in the synthesis gels from which zeolite materials are obtained, and to promote the surfactant assisted assembly of the

zeolite precursors present in the gel. This procedure results in materials where no zeolite XRD lines are commonly detected, and which have thermal stability higher than that of conventional mesoporous materials. This process is described in the following section.

2.1. Synthesis of ordered mesoporous materials from zeolite precursors

The materials obtained by using this procedure can be classified according to the nature of the zeolite precursor and surfactant, and the synthesis conditions, Table 2. The first steam-stable mesoporous material obtained following this synthesis procedure was reported by Pinnavaia et al. [30,31]. The authors described the synthesis of a hexagonal aluminosilicate mesostructure (Si/Al = 9), denoted as MSU-S, derived from seeds that normally nucleate the crystallisation of faujasite type Y. A critical step is the lowering of the pH of the seeds solution to a value of ~ 9 by addition of a solution containing sulphuric acid and the surfactant. It is claimed that the MSU-S material retains a well-ordered hexagonal structure upon steaming at $800\text{ }^\circ\text{C}$. Indeed, the activity of the steamed material in cumene cracking is higher than that of conventional Al-MCM-41, although the activity of both materials prior steaming is quite similar [52]. A similar synthesis strategy has

Table 2
Synthesis strategies using zeolite seeds or precursors

References	SDA	Surfactant	Conditions	Resulting materials	Reaction
[30,49,50]	No (FAU)	CTAB	Si/Al = 9; pH 9 by H_2SO_4	MSU S_{FAU}	Cumene cracking
[32,35]	TPAOH, TEOAH	CTAB	Si/Al = 67	MSU S_{MFI} , MSU S_{BEA}	Cumene cracking
[33,43]	TPAOH, TEOAH	P123 + TMB	Si/Al = 50; pH 4.5–6.5 by H_2SO_4 or pH < 2	MSU-S/ F_{FAU} MSU-S/ F_{MFI} , MSU-S/ F_{BEA} (Foams)	
[34]	TEAOH	Corn starch	Si/Al = 50	Al-MSU/AS	Cumene cracking
[36,37]	TEAOH	CTAB	Si/Al = 40	MAS-5	
[38–40]	TEAOH, TPAOH	P123	Si/Al = 40 and Si/Al = ∞ , pH < 2	MAS-7, MAS-9, MPS-9	Cumene cracking 1,3,5-tri-isopropylbenzene
[39]	TEAOH	P123	Si/Ti = 30, pH < 2	MTS-9	Phenol hydroxylation, and 2,3,6-trimethylphenol hydroxylation
[41]	TPAOH	P123	Si/Fe = 105	MFS-9	
[42]	No (zeolite L)	CTAB, P123	pH 10, pH < 2 (respectively)	MAS-3, MAS-8	Cumene cracking
[44,45]	TMAOH	CTAB	Si/Al = 2–3; pH > 12	ZPM	Xylene isomerisation
[46]	TPAOH	CTAB	Si/Al = 20–25 pH > 12		
[47,48]	TPAOH (NP)	CTAB	Si/Al = ∞	NP/CTAB (MCM-41)	
[51]	TEAOH	CTAB	Si/Al = 50	BM (MCM-48)	

ZSM-5 precursor is prepared with TPAOH as template, BEA from TEOAH, and zeolite Y from TMAOH. MCM-41 and SBA-15-like materials are prepared from CTAB and P123, respectively.

been used to obtain steam-stable mesoporous materials assembled from MFI and BEA seeds [32]. The activity of these materials in cumene cracking is three times higher than that of conventional Al-MCM-41, but no activity data have been reported so far for the steam-stable materials. Interestingly, the formation of mesostructured cellular foams from seeds of zeolites FAU, MFI and BEA at acidic pH by using Pluronic 123 has also been reported [33]. The calcined samples retain a fraction of tetrahedral aluminium in the framework much higher than that of samples prepared in the absence of zeolite seeds, and the retention of surface area after steaming is also remarkable. Thermally stable SBA-15 analogues have been also prepared from the same zeolite seeds, which show a much higher activity than conventional Al-containing SBA-15. Unfortunately, no information on catalytic activity of the steamed foams and SBA-15-like materials has been provided yet to the best of our knowledge.

Zhang et al. have reported the formation of ordered mesoporous aluminosilicates materials by assembling precursors of a variety of zeolites, like BEA, MFI, FAU and LTL, in the presence of either hexadecyltrimethylammonium (CTA) bromide at alkaline pH or Pluronic P123 at acidic pH. Table 2 summarises these results. These materials are claimed to possess a high resistance against severe treatment with water, as well as a catalytic activity much higher than that of conventional mesoporous materials. The enhancement of both stability and activity has been attributed to the use of pre-formed zeolite precursors [36], and a tentative hypothesis has been launched on the mechanism of formation of these materials, which would involve nanoclusters of zeolite containing primary and secondary building units [36].

Taking this hypothesis a step further, precursors of the colloidal zeolites FAU and MFI have been assembled at alkaline pH in the presence of CTA [44–47]. It is expected that the zeolite precursors leading to colloidal zeolites (regardless their chemical nature) would have an average size smaller than those present in conventional zeolite gels. The small size of the precursors would eventually facilitate their assembly in order to build up a stable framework of the mesoporous material. It is noteworthy that theoretical considerations on the stability of hexagonal mesoporous MCM-41-like structures suggest that the most favourable wall thickness would be around 1.0 nm [53,54]. In other words,

if the zeolite particles to be assembled are too large, the assembling process would not occur. These observations would lead to reconsider most of the reported procedures that claim to build the mesoporous framework from protozeolitic particles, as simple recrystallisation processes.

Differences in porosity are observed among materials obtained from colloidal MFI and FAU precursors. MFI precursors allow the formation of materials containing mesopores, while if FAU precursors are used, materials containing a high fraction of micropores are obtained. Ar adsorption indicates the presence of large micropores ($d_p \sim 1.4$ nm), in agreement with the TEM studies [44,45].

Catalytic activity of the calcined samples in *m*-xylene conversion indicates that a deep modification of the T–O–T connectivity exists in the vicinity of the protonic acid sites. The catalytic activity of some selected samples in this reaction has been compared with that of a commercial ZSM-5 (Si/Al = 15), USY catalyst (CBV 720, $a_0 = 2.428$ nm) and MCM-41 (Si/Al = 15). It can be observed in Fig. 1 that the *m*-xylene conversion of a sample derived from ZSM-5 precursors, synthesised at room temperature (Z3-9), is one third that of the reference ZSM-5. In general, the activity of the samples derived from colloidal faujasite precursors is nearly two orders of magnitude higher than that of Al-MCM-41. The overall catalytic behaviour distinguishes, in our opinion, the materials prepared by the procedures disclosed here from conventional ZSM-5 and USY zeolites, and strongly suggests that neither

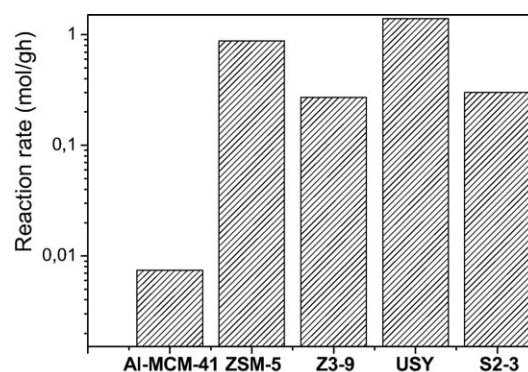


Fig. 1. Catalytic performance in *m*-xylene isomerisation. Some selected mesoporous samples prepared from ZSM-5 (Z3-9) and FAU (S2-3) precursors, are compared with a commercial USY (CBV 720, $a_0 = 2.428$), ZSM-5 (Si/Al = 25) and MCM-41 (Si/Al = 15) synthesised from conventional procedures. Reaction rate extrapolated at zero time ($\text{mol g}^{-1} \text{h}^{-1}$) at ca. 10% *m*-xylene conversion.

Table 3
Properties of calcined and steamed samples prepared from ZSM-5 precursors

Sample	d (Å)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Vo reac. ($\text{mol g}^{-1} \text{h}^{-1}$)
Z3-7 cal	39.3	1069	0.91	1.86E-1
Z3-7 cal ST		514	0.56	2.50E-2
Z3-9 cal	44.0	1196	1.29	2.73E-01
Z3-9 cal ST		534	0.74	3.28E-02

Z3-7 and Z3-9 have been prepared from ZSM-5 precursors aged for 5 and 24 h, respectively, prior to the addition of the surfactant solution [46].

ZSM-5 nor zeolite Y nanocrystals would eventually be building up the inorganic framework. The stability of the final catalysts was tested in steaming conditions. Materials prepared from ZSM-5 precursors at two different temperatures [46] appeared to be fairly stable under severe hydrothermal treatment (steaming at 100% humidity for 1 h at 700 °C). Even though the samples loose surface area and pore volume (Table 3), the meso-structure is retained (Fig. 2). The steamed catalysts still show reasonable activity in *m*-xylene isomerisation compared to the calcined ones (Table 3).

2.2. The role of zeolite precursors

Zeolite precursors have been thought to be useful as building blocks of mesoporous materials with crystal-

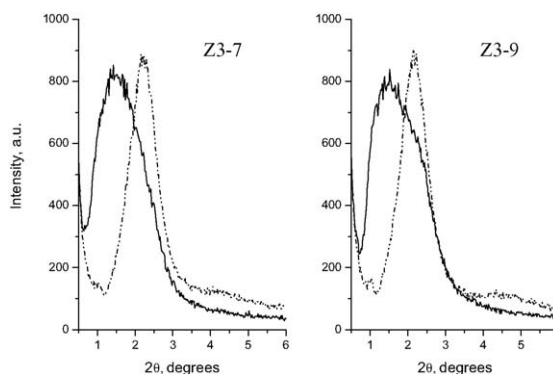


Fig. 2. X-ray diffraction pattern of samples prepared from ZSM-5 precursors after calcination (dotted lines) and further steaming treatments (straight lines). Steaming treatment: $T = 700$ °C for 1 h at 100% water vapour.

line walls due to their supposed ordered structure (Table 2).

Despite their colloidal nature, i.e. small particle size (less than 5 nm), zeolite precursors have been widely studied by different techniques, and many possible structures and growth mechanisms have been proposed [55–57]. However, it is not yet well understood whether those building units behave as bricks in the formation of zeolite crystals or dissolve and rearrange once adsorbed on the zeolite surface. It is out of the scope of this work to analyse the structure and possible behaviour of these precursors. However, it is worth to

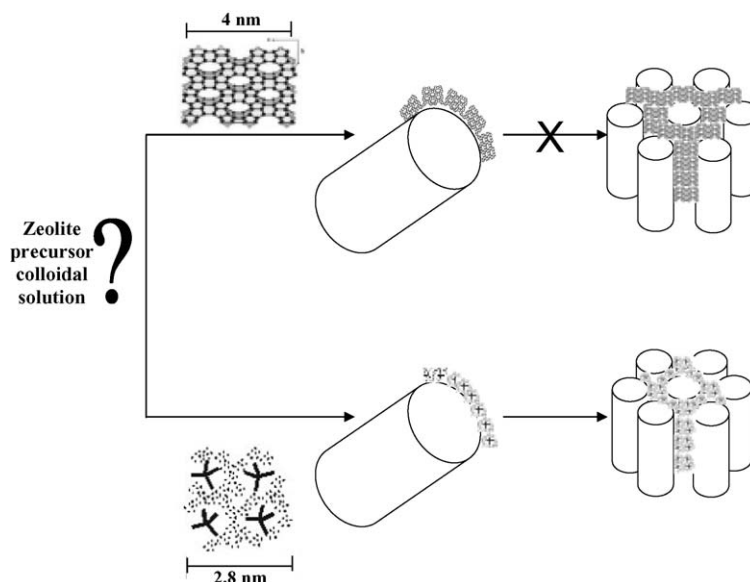


Fig. 3. Scheme of possible assembly of zeolite precursor with a micellar surfactant phase. Proposed structure of subcolloidal zeolite precursor nanoparticles have been adapted from Ref. [59]. Proposed TPA-mediated amorphous agglomerates have been adapted from Ref. [61].

mention that a more careful and deep understanding of zeolite precursor solutions is needed in order to succeed in the use of those chemical entities as building blocks of mesoporous materials. A few examples will serve to illustrate the complexity of this synthesis strategy.

Claims on the use of zeolite ‘seeds’ solutions are often found within this context, yet scarce evidences on the effective seeding behaviour of such solutions is actually supplied. Zhang et al. [36] mentioned the efficiency of their precursor solution in crystallising zeolite Beta, but no comparable information is found in like reports [32]. As an example, a zeolite Beta seeds solution is reported to be used for the synthesis of MSU-type materials, but careful inspection of the synthesis procedure reported for such solution reveals that it should contain nanocrystals of zeolite Beta in the range 10–100 nm [58].

Martens et al. tried to ‘tile’ zeolite precursors, which they named “nanoslabs”, to form a mesoporous mate-

rials. However, the curvature of a CTAB micelle is not favoured for the geometric packing of such large ($1.3 \times 4.0 \times 4.0$ nm) zeolite bricks [59,60]. In MCM-41 type materials, pore wall thickness is about 1 nm, and therefore it would be very difficult to accommodate those highly structured bricks (‘nanoslab’) into a highly condensed crystalline wall (Fig. 3 top). On the other hand, a proposed agglomeration of silica/template clusters that leads to amorphous 1–3 nm ‘primary units’ [61], fits better into the picture. A more flexible and dynamic units could accommodate better to the curvature of a surfactant micelle under the adequate conditions (Fig. 3 bottom). If this is the case, it is still necessary to find the synthesis conditions to nucleate and convert those small amorphous regions into crystalline zeolite-like walls. Under these circumstances, the factors involved in the thermal treatment of the solution containing both

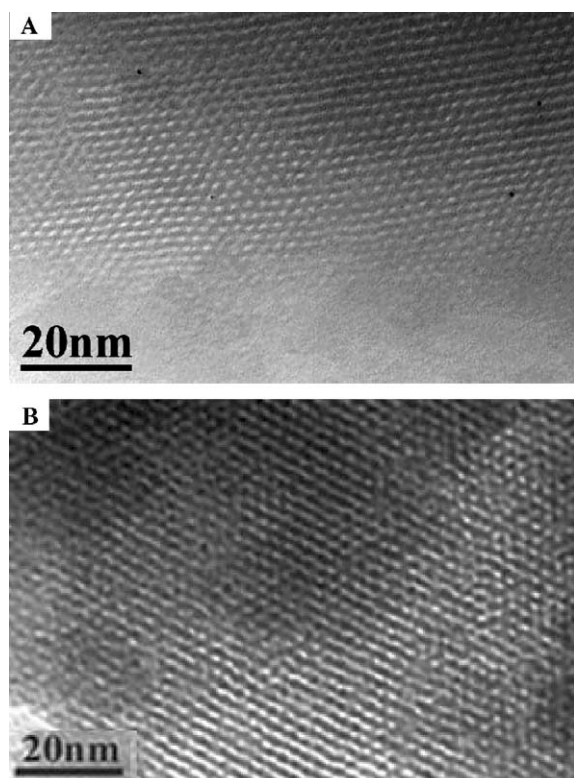


Fig. 4. TEM images of mesoporous materials obtained from zeolite precursors in our laboratory. As-made (A) and calcined (B) mesoporous materials prepared from FAU precursors.

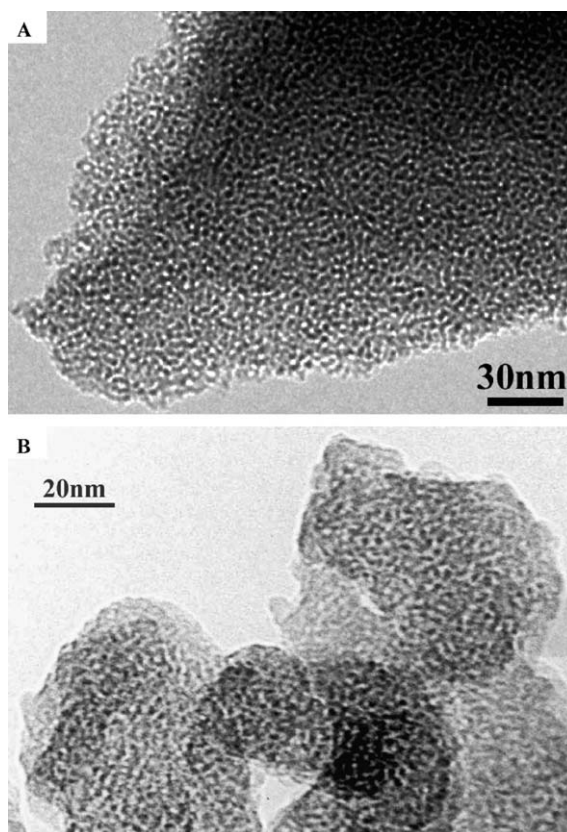


Fig. 5. TEM images of disordered mesoporous materials obtained from ZSM-5 precursors in our laboratory (Z3-7) (A). Disordered structure is also obtained for Al-MCM-41 (Si/Al = 15), shown for comparison purposes (B).

the zeolite precursors and the surfactant became of primary importance in the whole process.

Besides geometry considerations, it is necessary to think on chemical interactions too. A precursor formed with a cationic template at high pH should be regarded as a dynamic system in which the addition of a new cation (CTA) would compete for interacting with the silica. Slightly different pH and chemical interactions could lead to different final materials. In our experience, Faujasite and ZSM-5 precursor solutions, treated under the same basic conditions in the presence of a surfactant solution behave differently. The first one leads to hexagonal MCM-41-type mesoporous packing that loses some order after calcination (Fig. 4). The second one produces disordered mesoporous materials, as shown in Fig. 5A. Even though this type of mesoporous materials do not show a defined arrangement of pores (see XRD in Fig. 2), they present nevertheless a narrow pore size distribution in the mesoporous range, and the TEM images corroborates the

presence of disordered but homogeneous mesoporous structure. This type of disordered structure is commonly observed when rich Al-MCM-41 materials are prepared in one-step synthesis using CTAB as surfactant (Fig. 5B). Huang et al. [22] also observed a transformation of the hexagonal ordered MCM-41 toward a disordered structure when TPA cations seem to be incorporated in the walls. However, recently On et al. have found the same type of disordered mesoporous structure after treating mesoporous aluminosilicates synthesised from the triblock-copolymer Pluronic 123, with a TPAOH solution. After ageing at 130 °C, they obtained a two-phase material as shown by bright and dark field images [26]. In our case, the ZSM-5 crystals have not been observed at any stage of the crystallisation treatment. The Si/Al ratio estimated from XEDS analyses of over 20 disordered mesoporous particles is about 22, showing in all the cases a homogeneous distribution of aluminium. As an example, Fig. 6 shows the Si, O and Al mapping of one particle with disordered mesoporous

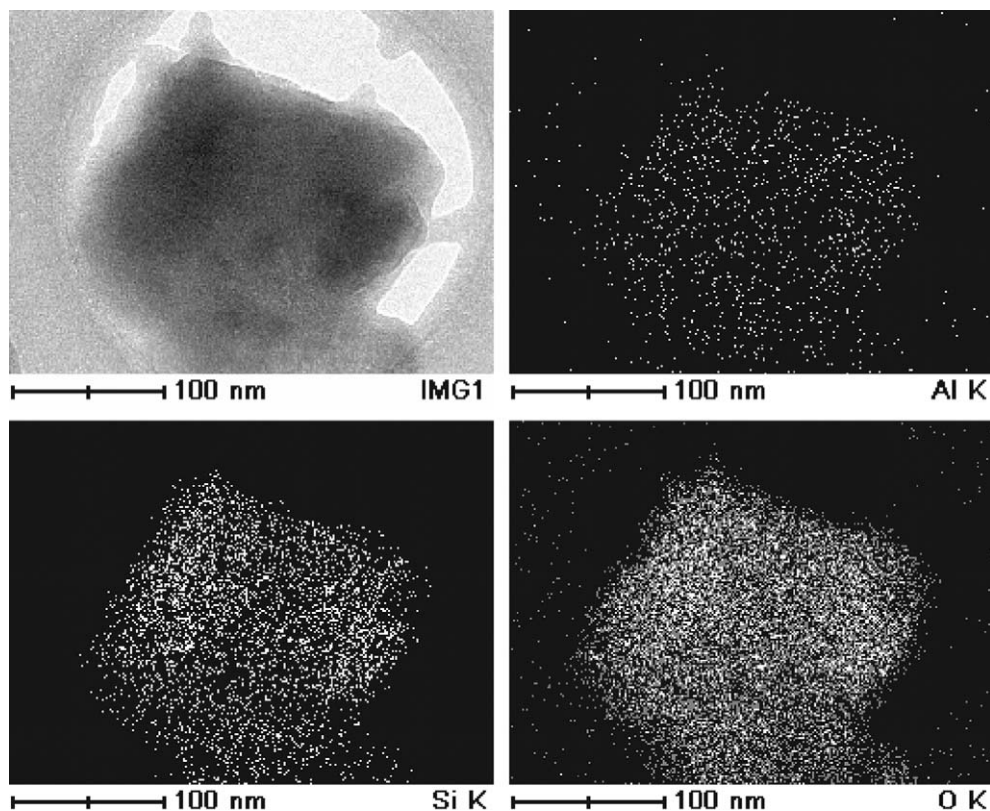


Fig. 6. Imaging and chemical composition of sample Z3-7 (ZSM-5 precursors) using a FE-TEM microscope (JEOL JEM 2010F) in STEM mode. Top right inset shows a homogeneous distribution of aluminium within the disordered mesoporous SiO₂ matrix (Si distribution in bottom left inset, and O in bottom right inset).

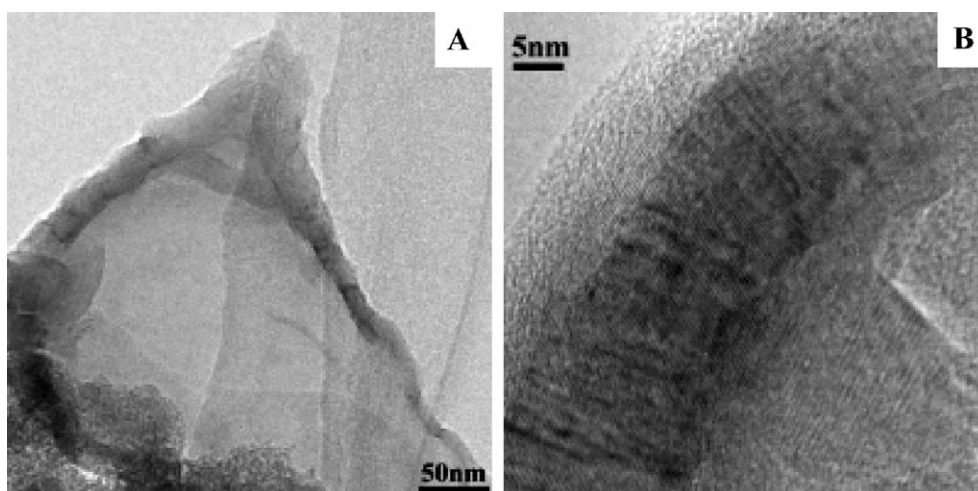


Fig. 7. HRTEM images of the vesicle-like particles with Si/Al = 1. Lower magnifications allows observing the vesicle type of particle (A), whereas higher magnifications (B) shows fringes with 4 Å d -spacing in the thick edges.

rous structure. It is also noteworthy that besides these particles, the same sample presents different and less abundant vesicle-like structures. These particles are observed in the material Z3-7 (aged for only 5 h at 80 °C) after calcination and show a Si/Al ratio close to 1. The vesicle-like morphology can be easily observed at low magnification in Fig. 7A, resembling some other vesicle-like morphology obtained in certain carboxylic acid–CTAB systems [62,63]. As in the mentioned references, the vesicle structures are surrounded by a thick shell, but the remarkable feature in these particles is the micro-lamellar structure (4 Å d -spacing) forming the surrounding layer (Fig. 7B). The stability under the electron beam of these particles along with its chemical composition could lead us to think that some lamellar aluminosilicate would be formed at the same time as the mesoporous structure.

Transmission electron microscopy (TEM) is currently used to elucidate the nature of the microporous/mesoporous structure along with the aluminium distribution. However, no evidence of crystalline wall either in images or diffraction patterns have been reported so far. Even more, it should be noted that no TEM images of colloidal zeolite precursors of less than 5 nm have been reported, therefore finding crystalline patterns within a 1–3 nm pore wall is not straightforward. After this analysis, it should be learnt that the zeolite precursor/surfactant systems are more complicated and difficult to analyse than it would be thought.

3. Perspectives

The long-range ordering of the TO₄ entities that build up the framework of ordered mesoporous materials is a much wanted objective. In spite of the development of several synthesis approaches, this goal remains still elusive. Success in this field will no doubt be dependent upon better understanding of the nature of the aluminosilicate entities present in zeolite-producing gels, as well as on the chemical interaction between these oligomers and amphiphilic molecules in solution. In our opinion, this research challenges our present knowledge of sol-gel chemistry and quasi-crystalline solids.

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