Synthesis of silicalite-1 by dry-gel conversion method: factors affecting its crystal size and morphology

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Abstract Silicalite-1 crystals were synthesized from clear and diluted solutions by the dry-gel conversion method and the hydrothermal method was used as reference to do a comparative study. The effect of the structure-directing agent, silica source, aging time and crystallization time was investigated. Zeolite crystals, about 200–500 nm and 1 micron, were obtained by the liquid phase hydrothermal (LPH) and steam-assisted crystallization (SAC), called as dry-gel conversion method, respectively. The crystals were identified by XRD and SEM. The results show that the aging time and the water content are crucial in the synthesis of zeolites. Indeed, well formed zeolite crystals are obtained by the SAC technique using a lower amount of water than in the LPH method. However, the presence of the structure directing agent (SDA) into the dry gel determines the crystallization of silicalite-1.

Keywords Silicalite-1 · Hydrothermal synthesis · Dry-gel conversion · Crystal size · Morphology · Structure directing agent

1 Introduction

Zeolites are hydrated aluminosilicates highly crystalline with pores of molecular dimensions. Synthetic zeolites present a wide range of pore sizes and topologies and they show high thermal, chemical, and mechanical stability. Zeolites have been successfully used in a large number of industrial applications such as catalysis, chemical separations, adsorption and ion-exchange [1–3]. The acid sites due to the presence of aluminium, the high specific surface and the well-defined pore dimensions have imposed them as selective catalysts [4–6].

The crystalline nature of zeolites is the basis to produce new materials like membranes. The regular microporous tridimensional network acts as a molecular sieve [7, 8]. In the last 200 years, around 40 types of natural zeolites have been identified; the most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, mordenite and phillipsite. There are *ca.* 150 types of synthetic zeolites, among them: zeolites type A, X, Y and MFI [9–11].

The MFI zeolite structure includes the ZSM-5 and the aluminum-free analogue, silicalite-1. The MFI structure has a two-dimensional pore system consisting of sinusoidal channels running in the [100] direction and intersecting straight channels running along the [010] direction. The pentasil family is included in the MFI framework topology, the framework structures are built from five-membered rings [12].

In 1978, for the first time, a new polymorph of silica (silicalite-1, refractive index 1.39, density 1.76 g cm^{-3}) was reported [13]. The fundamental building unit is a tetrahedron constituted by silicon and four oxygen atoms, TO_4. Silicalite-1 was found to have a novel framework enclosing a porous three-dimensional system of intersecting channels defined by 10-oxygen-atom rings wide enough to absorb molecules up to 0.6 nm in diameter [13]. The size of the pore openings is comparable to the size of the smallest organic molecules, and thus silicalite is suitable for a variety of industrial separations [14].

Since the aluminum-free silicalite lacks ionic sites, it has hydrophobic properties and preferentially adsorbs organic

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molecules such as low molecular weight hydrocarbons small enough to enter the pore openings [15]. The most common method to prepare silicalite-1 is the hydrothermal crystallization from a relatively simple mixture of tetra-propylammonium ions (TPA$^+$) acting as template, sodium hydroxide as a mineralizing agent, a silicon source, and water under autogenous pressure, at temperatures ranging from 100 to 250 °C [16, 17]. It is usually accepted that the template promotes the formation of the oligomeric silicate precursor species that, later, form the final MFI framework. However, in 1990, Xu et al. [18] reported for the first time a new technique to crystallize an amorphous aluminosilicate dry gel. An aqueous organic vapor to form zeolites is introduced in the mixture as a mean to reduce the consumption of organic materials used as structure directing agent (SDA) during the crystallization step. This synthesis method is now generally referred to as vapour phase transport (VPT) [19]. Matsukata et al. [20] followed this procedure to prepare ZSM-5, ferrierite, mordenite and analcime, but, to our knowledge, it has not been tested in the synthesis of silicalite-1 synthesis. Note that in such a synthesis the dry gel already contains the templating agents. Steam is only supplied by the vapor phase. This method is known as steam-assisted crystallization (SAC). These two routes are referred as dry-gel conversion (DGC) methods. The DGC method has many advantages compared with the classical hydrothermal crystallization technique. For instance, it allows the preparation of all-silica zeolites and it reduces the synthesis time as well as the consumption of expensive templates [20]. Additionally, the DGC method offers the possibility to prepare zeolite membranes on a broad variety of supports [19, 20]. We have recently shown that small crystals (200–500 nm) of LTA zeolite can be obtained from diluted solutions without organic template using a conventional hydrothermal method [11]. Schoeman et al. have reported on the effects of some important parameters on the colloidal and nano-sized zeolite synthesis [21–23]. In the present work, the

hydrothermal and the dry-gel conversion (VPT and SAC options) methods were used to crystallize silicalite-1. Aging time in both synthesis methods is compared. The samples were prepared to explore the effect of the silicon source (colloidal or fumed silica), the aging time and the addition of organic template on crystallite size and morphology.

2 Experimental

2.1 Gel preparation

The precursor gels were prepared using sodium hydroxide (NaOH, Fluka), distilled water and tetrapropylammonium bromide (TPABr, Aldrich) as SDA. The silica source was either colloidal silica (Ludox AS-40, Aldrich) or fumed silica (Aerosil 300, Degussa). The gel composition (molar ratio) of each of the prepared gels is presented in Table 1.

The obtained products were labelled as Sili-1 (crystallized by the hydrothermal method [24], using ludox AS-40 as a precursor). The samples Sili-2, Sili-3 and Sili-4, were crystallized by the SAC method, using two different silica precursors, for Sili-3 ludox AS-40 was used, and for the samples Sili-2 and Sili-4 fumed silica was used. Lastly, another gel was prepared [25], but without SDA. The resulting samples were labelled as Sili-5, Sili-6 and Sili-7 (crystallized by VPT option). The preparation of the Sili-1 to Sili-4 gels was carried out as follows. First, the required amounts of NaOH and TPABr were dissolved in distilled water (solution one) under stirring, in a polypropylene (PP) bottle. In a second PP bottle, a silica solution was prepared with the corresponding silica source (solution two) and water under stirring. Then, the solution one was slowly added to solution two, under vigorous stirring for 2 or 3 h, until a clear solution (Ludox) or a diluted silicate (fumed silica) solution were obtained. The precursor solutions were aged under stirring in two steps, first they were aged

Table 1 Gel composition to preparing precursors gel and conditions used to crystallize zeolites and obtained compounds

Sample	Gel composition (molar ratio)				Silica source	Crystallization method	Crystallization time (h)	Phase (XRD)
	SiO$_2$	NaOH	TPABr	H$_2$O				
Sili-1	14	3	1.0	788	Ludox	HT[a]	24	Silicalite
Sili-2	44	3.7	52	788	Aerosil	SAC[b]	24	Silicalite
Sili-3	21	3	1.0	788	Ludox	SAC	24	Silicalite
Sili-4	44	3.7	52	788	Aerosil	SAC	24	Silicalite
Sili-5	10	0.22	–	280	Ludox	VPT[c]	24	Non-crystalline silica
Sili-6	10	0.22	–	280	Ludox	VPT	72	Non-crystalline silica + quartz
Sili-7	10	0.22	–	280	Ludox	VPT	120	Quartz

The aging time was 7 days and the temperature of synthesis was 170 °C for all samples

[a] HT: Hydrothermal, [b] SAC: Steam-assisted crystallization, [c] VPT: Vapour phase transport

for 24 h to observe the gel stability and, then, the aging was continued for 6 days more. Thus, 7 days was the total aging time for all samples.
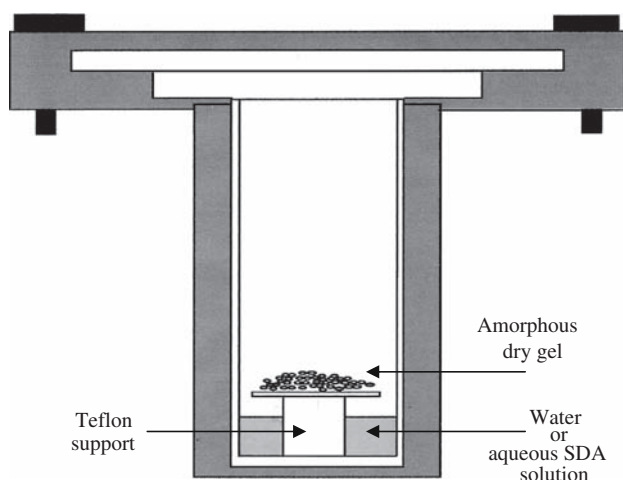
2.2 Zeolite crystallization

2.2.1 Liquid phase hydrothermal method

The clear solution was transferred to a Teflon-lined stainless steel autoclave with a volume of 100 cm^3. The zeolites were crystallized hydrothermally for 24 h under static conditions in a convection oven preheated at 170 °C. The obtained zeolite powder was rinsed with distilled water and calcined for 4 h at 450 °C to remove the tetrapropylammonium template occluded in the zeolite pores. For comparison purposes, only the sample Sili-1 was synthesized following the liquid phase hydrothermal method. It was then used as reference and could be compared to the dry gel method.

2.2.2 DGC methods

The samples Sili-2, Sili-3 and Sili-4 were crystallized through the SAC method. First, a silicate gel aliquot was dried into a furnace at 100 °C to obtain an amorphous dry gel (0.4 g). Then, the amorphous dry gel was put in a Teflon support (Fig. 1) into a Teflon-lined stainless steel autoclave. Then, five cm^3 of water were introduced in the autoclave bottom. The reaction was carried out for 24 h under static conditions in a convection oven preheated at 170 °C. At this temperature, water is steam, and hence it is in contact with the dry gel. After the crystallization step, the samples were treated in the same way as the sample prepared by the hydrothermal method (Sili-1).

The samples Sili-5, Sili-6 and Sili-7 were synthesized following the VPT method. The crystallization methodology was the same as in the SAC method, but it is important to mention a fundamental difference between these methods. In the SAC method the SDA (TPABr) was incorporated to the dry gel, and in the VPT method the dry gel did not contain SDA (TPABr). To crystallize these samples, dry gels were put in a Teflon support, as in the SAC method, but, in the autoclave, an aqueous SDA (5 mL, 0.05 M) solution was poured, instead of just water as in the SAC method.

2.3 Characterization

The structure of silicalite-1 was determined by X-ray diffraction (XRD, Bruker, D8 Advance) using Cu Kα radiation, with a step size of 0.02° per second from 5° to 40° on the 2 theta scale. The morphology was observed by scanning electron microscopy (SEM, Leica Stereoscan 440 microscope); the samples had to be covered with gold to avoid charge problems.

3 Results and discussion

3.1 XRD characterization

Figures 2 and 3 present the XRD patterns of silicalite-1 synthesized by the liquid-phase hydrothermal (LPH) and steam-assisted crystallization (SAC) methods, respectively. All diffraction peaks are sharp and narrow indicating the formation of a silicalite-1 (JCPDS #48-0136 card) with high crystallinity, no other compounds were identified. Figure 4 displays the XRD patterns of samples prepared by the vapor-phase transport (VPT) method. No zeolite was

Fig. 1 Dry gel crystallized into Teflon-lined stainless steel autoclave
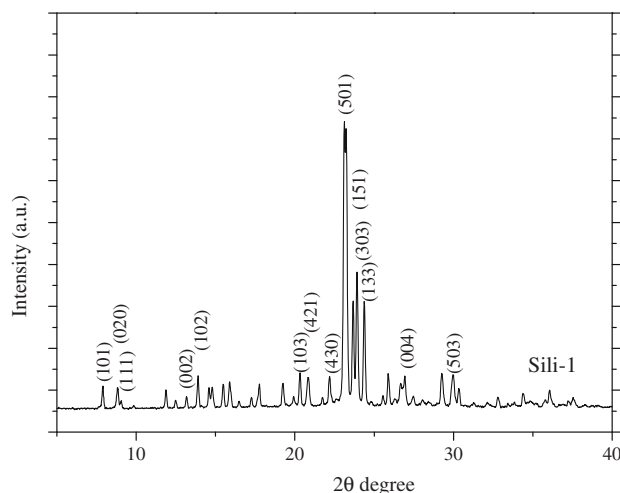
Fig. 2 XRD pattern of silicalite-1 obtained by hydrothermal method
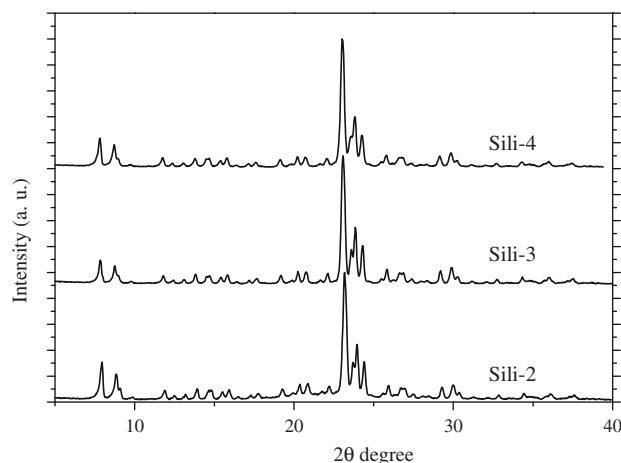
**Fig. 3** XRD patterns of silicalite-1 obtained by SAC method
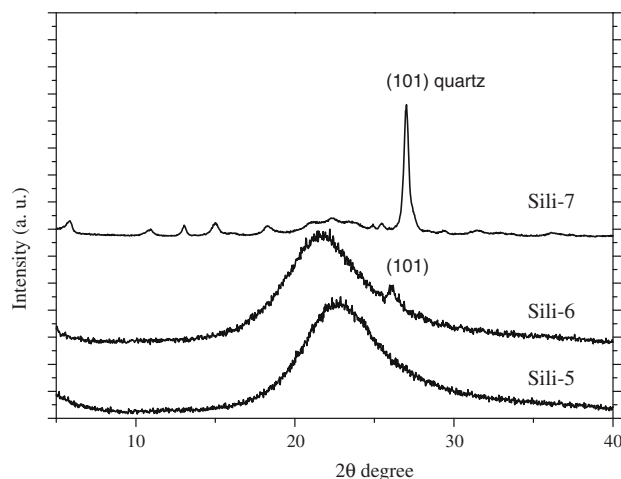
Fig. 4 XRD patterns of materials obtained by VPT method, only Sili-7 crystallized and the others samples formed a non-crystalline phase

formed, only amorphous silica (Sili-5 and Sili-6) or quartz (Sili-7) was observed, depending on aging and synthesis time, as shown in Table 1.

3.2 SEM characterization

The XRD results corresponding to the samples shown in Figs. 2 and 3, synthesized with both methods, were confirmed by scanning electronic microscopy. This technique was used to determine the morphology and the particle size. In the zeolite synthesized through the liquid phase hydrothermal method, Fig. 5, the particles were more dispersed and aggregates were not found. The average size was 500 nm approximately, still, other sizes, in the range 200 to 300 nm, were also observed. A hexagonal morphology, typical of MFI zeolites, is clearly observed. Figure 6 corresponds to the SEM micrographs of SAC samples (Sili-2 and Sili-3). If compared to MFI typical
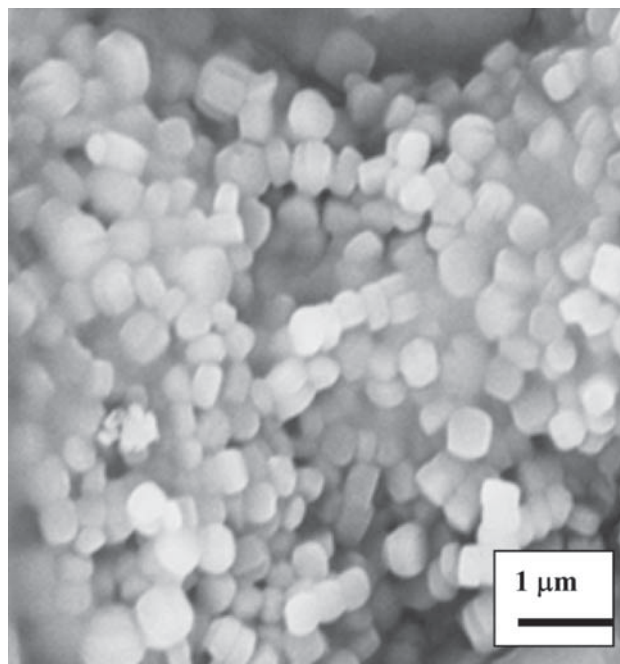

Fig. 5 SEM image showing crystallites of silicalite-1 obtained by hydrothermal method (Sili-1)

zeolite shape, aggregates of smaller and slightly different particles can be observed. Sample Sili-2 shows bigger crystals than sample Sili-3, where the mean size is around 1 μm, the size is smaller than the crystal size obtained by Matsufuji et al. [26]. These authors reported a crystal size of 10 μm in their ZSM-5 zeolites synthesized through the SAC method. Note that the only difference between silicalite and ZSM-5 (silicalite-1 with Al) is the aluminium content that promotes an easier crystallization of this zeolite even without an organic template [11, 27].

4 Discussion

We synthesized silicalite-1 by the LPH and SAC methods using templates in both cases. Silicalite-1 was not formed by the VPT method by two reasons. One of them could be the used SDA quantity which was not enough to crystallized the silicalite phase. The other reason was that the type of SDA (TPABr) used in this work; it is not a volatile organic compound. The crystallization temperature is low and it is not possible to form TPA^+ cations that interact with silica tetrahedral. Table 1 summarizes the synthesis conditions to obtain the specified compounds. The hydrothermal method (Sili-1) as well as the SAC method (Sili-2, Sili-3 and Sili-4) provided silicalite-1 after 24 h of crystallization independently of the type of silica source. Although, when fumed silica is used as silica source larger crystals were obtained. Instead, if the VPT method is

Fig. 6 SEM image showing crystallites of silicalite-1 obtained by the SAC method (**a**) Sili-2: aerosil, (**b**) Sili-3: ludox, as silica source respectively
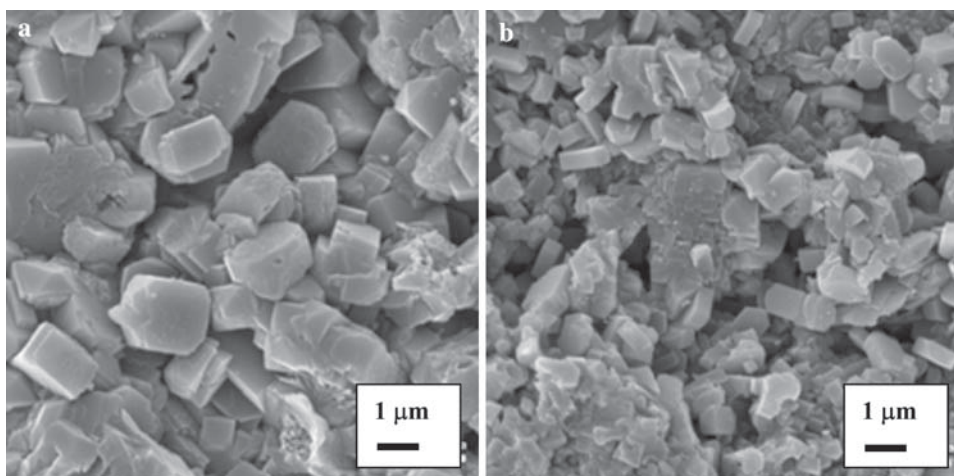
followed, after the same crystallization time, no zeolite was obtained (Sili-5); the resulting compound turned out to be non-crystalline silica. When the crystallization time was increased up to 72 h, silica began to crystallize as quartz and, after 120 h, the quartz phase is the only one observed. This result is similar to the result reported in reference [28] where 7 days of crystallization time were used at 175 °C, but, in this work, the crystallization time was only 24 h and the gel was previously aged for 7 days. According to the above mentioned results, to crystallize an amorphous gel, it is clear that the aging time is more important than the crystallization time [11, 29]. This result is important because it shows that it is possible to prepare thin films on a porous support. Then, zeolite membranes without defects can be prepared where the mass transport and diffusion should be faster than on zeolite membranes with crystals bigger. It is well known that homogeneous nucleation has a negative effect on the hydrothermal synthesis methods of membrane preparation [30]. In this case the dry-gel conversion methods can be employed to reduce the influence of the homogeneous nucleation during the preparation of the zeolite membrane [31].

Therefore, both methods (LPH and SAC) can be used to synthesize zeolites depending on the required crystal size. Using the hydrothermal method, a clear solution incorporates more water, propitiating a higher dispersion of the nuclei which do not agglomerate during the crystallization step. If the SAC method is applied, water is eliminated, and a fully dried gel is obtained where some nuclei may agglomerate and grow during the crystallization step.

To summarize our results we have shown the differences in the obtained product varying the crystallization method (LPH, SAC, VPT), silica source (ludox or aerosil), aging time (7 days) and crystallization time (24–120 h). On the one hand, the silica origin was not relevant, on the other, the template effect was crucial for the morphology of the obtained silicalite. Indeed, the SAC method promotes the formation of larger crystals than the liquid phase hydrothermal method. However, we obtained a crystal size close to 1 micron or less using SAC method. This result can be attributed to aging time instead of the time of crystallization or synthesis temperature. That correlation is well known for the traditional hydrothermal method, reported by Schoeman and co-workers. [32–34], but not for the dry gel method. Last but not least, the VPT experiments using were not appropriate to obtain silicalite-1 within 24 to 120 h as crystallization time. If the gel was aged for more than 7 days, it was possible to obtain silicalite-1.

In other syntheses, as the LPH, the silica source choice and the aging time determined the particle size. Instead in the SAC method, the particle size remained the same if the aging time was short (1 day) but if the aging time was increased, the crystal size tended to reduce, most probably because the template effect is not the determining step for the crystallite size and the morphology. The silica polymers, initially formed from each one of the reactants, interact homogeneously, in the same way, with the template. Therefore, the polymer density is not determinant.

Water amount in both synthesis methods (SAC and VPT) determines the crystallization mechanism. If water is mixed previously with the silica and the templating agent (SAC method), zeolite is formed, because in the dry solid some amount of water, around, 20–22 wt %, is maintained into the structure [16]. Whereas if water is mixed with the template and added to silica (VPT method), a non crystalline compound results. Thus, water may interact with the template, the silicate seeds are, then, formed. This hypothesis is supported by the results provided by the VPT synthesis. In this procedure, although the template mixed with water is present, the seeds are already formed and amorphous silica is obtained. Therefore, in this case, there is no interaction among the reactants. It seems, then, that

once the seed (silicalite with SAC or silica with VTP) is formed the direction of the synthesis is determined through a crystal growth mechanism.

In the liquid phase hydrothermal synthesis the crystallite size is very small (ca. 500 nm) if compared to the SAC method which provides 1,000 nm particles. This difference can be attributed to the diluting effect of water. Most probably, in the liquid phase hydrothermal preparation, more nuclei are formed. Hence their growth is limited and crystals do not associate. In the SAC method only some nuclei are built, they grow slowly and are able to agglomerate due to water elimination.

5 Conclusion

In this work, crystals of silicalite-1 were obtained from diluted solutions, using two different methods, one of them was the traditional liquid phase hydrothermal method, used as reference, and the other one was the steam-assisted crystallization (SAC). The zeolite crystals obtained by the liquid phase hydrothermal method were smaller and more dispersed. This feature has to be attributed to the use of clear solutions as precursors, as reported by others authors. In SAC route, crystals *ca.* 1 micron size were obtained, they are small for this crystallization method. Such a small size was attributed to aging time. The formed crystals agglomerated, as the dry gel is obtained previously to the crystallization step. SAC method is an alternative to synthesize zeolite with a lower amount of water independently of the silica source. The crystal size can be controlled through the synthesis method. Therefore, the formation of the thin films required in membranes or the filling of mesopores present in support materials can be proposed.

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