Solvent-free synthesis of zeolites: new insights into the mechanism and non-mechanochemical route
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Abstract

The solvent-free (SF) synthesis is a green alternative to the conventional method of synthesis for zeolites. In this study, we show for the first time the feasibility of carrying out the SF synthesis of silicalite-1 (F$^-\text{route}$) without any grinding. We also monitor the changes during the synthesis thanks to multiple characterization techniques: XRD, TGA, SEM, EDX, and multinuclear NMR ($^{13}\text{C}$, $^{19}\text{F}$, $^{29}\text{Si}$). We show how the duration of the thermal treatment impacts the zeolite crystal size and morphology, as well as the local degree of order probed by solid-state NMR. The obtained results provide new insights on the SF formation mechanism based on solid phase transformations. Our findings also show that once the organic structure directing agent (OSDA), here tetrapropylammonium, is incorporated, the crystals are formed and no other intermediate phases incorporating the OSDA exist. Further, we study the role of water in the synthesis using $^{17}\text{O}$ NMR. For this purpose, we develop a simple and efficient $^{17}\text{O}$ enrichment method of zeolite frameworks. The efficiency of this enrichment demonstrates the role of water in the hydrolysis and condensation reactions and its need for a successful synthesis.

Keywords: Zeolites, Solvent-free synthesis, Solid-state NMR spectroscopy, $^{17}\text{O}$ isotope labelling

1. Introduction

Zeolites are conventionally synthesized using the hydrothermal method (HT) in which water is used as a solvent for the reacting precursors [1,2]. Since the HT method involves the use of high...
temperatures and high pressures for long periods of time, other sought synthesis methods [3] have emerged as greener and more economical alternatives such as the ionothermal method [4,5], the microwave-assisted synthesis [2,5], and the solvent-free (SF) synthesis [5,6].

Compared to the HT method, the SF method has many advantages [5–10]. It is a simple method that might require only a grinding step prior to the thermal treatment duration [7], and produces less wastewater than the HT method. Another benefit linked to the use of the SF method is the increased production since more reactants can be introduced in the solvent’s place. It is also important to highlight the difference between the dry gel conversion (DGC) method and the SF method. The DGC requires dissolving the precursors which is to be dried later on before the start of the hydrothermal treatment [11,12]. This complicates the synthesis procedure and eventually large amounts of water are used as well.

The SF method was first reported by Meng, Xiao and co-workers [7] who used sodium metasilicate nonahydrate, fumed silica, ammonium chloride, and tetrapropylammonium bromide (TPABr) for the synthesis of silicalite-1 without the use of a solvent. The simple synthesis method consisted only of grinding the precursor powders for 10-20 min followed by heating at 180 °C for 1-2 days. In another publication [13], the same group reported the successful synthesis in the presence of F (NH4F). In further investigations on the method, Xiao et al. [12] highlighted the role of water in the synthesis as a catalyst but also stated the possibility to synthesize the zeolite in the absence of water [13]. Wang et al. described the difficulty to crystallize in the absence of water and reported an optimal 1.04 molar ratio of H2O/SiO2 for the synthesis powder (SiO2:0.15NH4F:0.035TPABr) [14]. The differences in literature could be a reason of not drying the precursors prior to the synthesis. Studies, associated to the mechanochemistry [15–17], were also conducted to understand the possible pre-synthesis reactions taking place during the grinding along with studies on optimizing the ideal parameters for this step [17,18].
In this work, we further investigate the SF method for zeolite synthesis. We monitor the changes in the synthesis powder during the thermal treatment for periods comprised between 1 h and up to 28 days (beyond reaching the fully crystalline phase). A combination of characterization techniques (XRD, SEM, $^{13}$C, $^{19}$F and $^{29}$Si solid-state NMR) brings new information on the mechanisms of formation. Besides that, we show for the first time that the solvent-free method can be carried out without any mechanochemical activation of the initial precursor. This removes the main obstacle in applying SF synthesis industrially since the current zeolites synthesis configurations are not designed for mechanical mixing of solids. Our study also helps understanding the role of water in zeolites synthesis by employing $^{17}$O enriched water in the synthesis. This enrichment method serves as a direct and simple alternative for isotopically enriching zeolite frameworks.

2. Experimental section

2.1. Materials

Silica gel ($\text{SiO}_2$, high purity Sigma-Aldrich), fumed silica ($\text{SiO}_2$ 0.2-0.3 $\mu$m powder, Sigma), tetrapropylammonium bromide (TPABr) ($\text{C}_{32}\text{H}_{70}\text{BrN}$, Merck KCA 99% minimum purity), ammonium fluoride ($\text{NH}_4\text{F}$, AlfaAesar 98% minimum purity) and $^{17}$O-labelled water ($\text{H}_2^{17}\text{O}$, CortecNet, 39.3%) were used as received. Demineralized water was obtained from exchange resins.

2.2. Synthesis of Silicalite-1

**Solvent-free synthesis**

The synthesis method was adapted from literature [13,14] by modifying the amount of the organic structure directing agent (TPABr) and varying the grinding and thermal treatment
durations. The amount of TPABr was introduced in excess (TPABr/Si molar ratio > 0.042) since TPABr is soluble in water and can be removed by a simple washing step after the crystallization.

Silica gel (SiO$_2$), TPABr, and NH$_4$F were dried in a 353 K oven overnight. Then the reactants were added in an agate mortar with molar ratios of 1SiO$_2$:0.08TPABr:0.15NH$_4$F:1H$_2$O (3.2 g of silica gel used). To study the effect of grinding time, four different samples were synthesized with grinding the reactants manually for 0, 1, 5, and 15 minutes at room temperature. The powder was transferred to a 45 ml Teflon vessel and sealed in a stainless-steel autoclave. The autoclave was placed in an oven at 448 K for 13-15 h. The obtained zeolites were washed, vacuum filtered, and after that were dried at 353 K overnight.

Samples synthesized without any grinding were prepared using the same above-mentioned method, with or without mixing the reagents using a spatula, with a thermal treatment of 1-14 d. Fumed silica was used as a Si source for the sample used to compare with the HT synthesis.

To investigate the evolution with the thermal treatment duration, the same procedure was followed using 15 min of grinding and with heating for different periods up to 28 days.

**Synthesis with $^{17}$O-labelled water**

The same synthesis protocol was followed but with scaling down the quantity of reactants by a factor of 9 (356 mg of silica gel). To minimize the contact with the atmosphere, the grinding/mixing step was replaced with shaking in a closed system using Retsch Mixer Mill 400 apparatus (MM400). The reactants powder was placed in a 10 ml stainless-steel jar followed by the addition of 110 µl water (using $^{17}$O-labelled water instead of demineralized water). The jar was shaken with 25 Hz speed for 5 min (no beads placed inside the jar). The powder was then transferred to a 5 ml Teflon chamber and sealed in a stainless-steel autoclave to start the thermal treatment. The autoclave was heated in a 448 K oven for 2 days. The product was washed with abundant amount of demineralized water, vacuum filtered, and finally vacuum-dried. The final synthesis yield was ca. 79% (320 mg of dried powder recovered after filtration).
Hydrothermal F-route synthesis

The required amount of water (24 g) corresponding to the equivalent molar ratio of 1SiO$_2$:0.08TPABr:0.15NH$_4$F:20H$_2$O was placed in a 45 ml Teflon chamber. Then, the specified amounts of dried TPABr and NH$_4$F were added. The solution was stirred with a magnetic stirrer until complete dissolution of solids. Fumed silica (4.0 g) was added to the solution and mixed with a spatula to form the precursor gel. The reactor was sealed in a stainless-steel autoclave to start heating at 448 K for 14 days. The obtained zeolite was washed, vacuum filtered, and dried in a 353 K oven overnight.

2.3. Characterization

Powder X-ray diffraction patterns (PXRD) were collected with Bruker AXS D8 diffractometer using Cu Kα radiation (1.5406 Å wavelength). The diffractometer measured the peaks with an angle (2θ) range from 5° to 60° and a step size of 0.02. The crystallinity percentage was calculated using the integral method: the area of the crystalline peaks is divided by the total area of the XRD pattern (see section S4 in SI).

Scanning Electron Microscopy (SEM) images were collected with a HITACHI 4800 S microscope using platinum coating on the samples (< 50 Å) prior to the observation. Energy dispersive X-ray (EDX) analysis was performed along with SEM analysis.

Thermogravimetric analysis (TGA) was done using NETZSCH TG 209 with alumina crucibles from 40 to 900°C at a 10°C/min heating rate under air.

$^{13}$C NMR cross polarization (CP-MAS) spectra were recorded on a Varian 300 (7.0 T) spectrometer ($
\nu_0[^{13}C] = 75.5$ MHz) with 7.5 mm rotors ($\nu_{\text{MAS}} = 5$ kHz), using 5 ms contact time, 5 s recycle delay and $^1$H decoupling during acquisition (50 kHz nutation frequency). TMS (tetramethylsilane) was the reference of the chemical shifts. Adamantane was used as an external secondary $^{13}$C reference ($\delta = 38.5$ ppm for the high frequency peak).
\(^{17}\)O NMR spectra were recorded on a Varian 600 (14.1 T) spectrometer \( (\nu_{\text{mas}}^{\text{17}O} = 81.3 \text{ MHz}) \) with 3.2 mm rotors \( (\nu_{\text{mas}} = 18 \text{ kHz}) \). The single-pulse spectrum was recorded using \( \pi/6 \) pulse (2 \( \mu \text{s} \) pulse width) and 0.5 s recycle delay with a 1024 total number of scans. The two-dimensional (2D) \( z \)-filtered multiple-quantum \(^{17}\)O MQMAS spectrum \([19,20]\) was recorded using triple-quantum (3Q) excitation and reconversion pulses of 3.3 and 1.1 \( \mu \text{s} \) lengths, a third transition selective pulse of 12.0 \( \mu \text{s} \) and with a \( z \)-filter delay of 5 \( \mu \text{s} \). The recycle delay was 0.25 s and the total number of scans was 2400. \(^{17}\)O chemical shift was referenced using \( \text{D}_2\text{O} \) \( (\delta = -2.7 \text{ ppm}) \) which corresponds to tap water at 0 ppm.

\(^{19}\)F NMR spectra were recorded on a Varian 600 (14.1 T) spectrometer \( (\nu_{\text{mas}}^{\text{19}F} = 564.7 \text{ MHz}) \) with 2.5 mm rotors \( (\nu_{\text{mas}} = 20 \text{ kHz}) \) or 3.5 mm rotors \( (\nu_{\text{mas}} = 18 \text{ kHz}) \), using \( \pi/2 \) pulses of 4 \( \mu \text{s} \) pulse width, and 5 s recycling delay. \( \text{CFCl}_3 \) was the reference of the chemical shifts. Polytetrafluoroethylene (PTFE) \( (\delta = -122.3 \text{ ppm}) \) was used as a secondary reference.

\(^{29}\)Si NMR cross polarization (CP-MAS) spectra were recorded on a Varian 400 (9.4 T) spectrometer \( (\nu_{\text{mas}}^{\text{29}Si} = 79.5 \text{ MHz}) \) with 7.5 mm rotors \( (\nu_{\text{mas}} = 5 \text{ kHz}) \), using 20 ms contact time, 5 s recycle delay and \(^1\)H decoupling during acquisition (50 kHz nutation frequency). Transverse relaxation times \( T_2' \) were measured using a CP-MAS block chained by a spin echo with \(^1\)H decoupling. TMS was the reference of the chemical shifts. Octa(dimethylsiloxy)-octasilsesquioxane \( (\text{Q}_8\text{M}_8\text{H}) \) was used as a secondary reference \( (\delta = -2.25 \text{ ppm}) \) for higher frequency resonance.

3. Results and Discussion

3.1. Effect of grinding

In a first set of syntheses, we varied the grinding time from 0 to 15 min while maintaining a constant thermal treatment duration (13-15 h) to study its effect on the crystallinity and the crystal size. From the XRD patterns we can detect characteristic Bragg peaks of the orthorhombic
phase \textit{Pnma} of silicalite-1 (MFI topology) crystals along with some scattering related to the presence of amorphous phases (Fig. S1). The crystallinity degree improves with introducing and prolonging the grinding step, achieving a fully crystalline phase with 5 min grinding (Fig. 1a). Only mixing the reactants without any grinding still yields crystalline MFI product but without fulfilling a full crystallinity (Fig. S1 and Fig. 1a). Hence, the grinding step is crucial to ensure obtaining a totally crystalline product in a short period but not essential for the synthesis to work. In fact, when increasing the thermal treatment to 24 h, a fully crystalline sample was obtained by only mixing the reactants without grinding (Fig. 2a-b). The synthesis is also achievable in 48 h by simply placing the reactants in the Teflon chamber and without any previous mixing nor grinding (Fig. 2c-d). Therefore, the solvent-free synthesis can be carried out without any mechanochemical step, which renders it more flexible.

Fig. 1. a) Crystallinity degree and average measured crystals lengths as a function of grinding time, b) TGA weight loss (experimental/theoretical) and crystallinity degree percentages as a function of grinding time. SF samples were synthesized after heating at 448 K (13-15h) with varying the initial times of manual grinding (0, 1, 5, and 15 min). The relative errors for the crystallinity degree and the weight loss ratios are estimated to be ±5% and ±2%, respectively.

Another observation for the impact of the grinding step on the outcome of the synthesis is the obtained crystal sizes. Grinding the initial precursor for longer periods yields smaller crystal sizes
as observed by SEM (Fig. 1a). 15 min grinding reduced the crystals length by around 70% when compared to only mixing. Prolonged grinding ensures the proper mixing of the reagents and reduces the particles size of the precursor. In turn, this could increase the nucleation rate yielding smaller crystals. The relationship shown in Fig. 1a could thus be further exploited for controlling the crystal sizes when using the SF method.

![SEM image of zeolite sample synthesized with only mixing](image1)

![XRD pattern of zeolite sample synthesized with only mixing](image2)

![SEM image of zeolite sample synthesized without any mechanochemical step](image3)

![XRD pattern of zeolite sample synthesized without any mechanochemical step](image4)

The TGA was also carried out to further characterize the SF samples synthesized with different initial grinding times. The TGA curves show a single mass loss around 693 K that would mainly correspond to the removal of TPA and F in the as-synthesized samples (Fig. S2), conforming to what has been published regarding MFI zeolites [21]. From these curves, we can also obtain the experimental/theoretical % (wt./wt.) weight loss ratios by assuming a fully crystalline silicalite-
zeolite $\text{Si}_{96}\text{O}_{192}\text{F}_4(\text{TPA})_4$ for the theoretical value. These ratios follow the same trend as the crystallinity percentage (Fig. 1b). This suggests that there are no other amorphous species containing the OSDA or $\text{F}^-$. $\text{^{13}C}$ NMR also confirms the existence of only TPA inside the MFI framework (Fig. S3).

The above-mentioned results were completed with NMR experiments. We observed that the grinding period does not affect the spectral resolution of $\text{^{29}Si}$ (if not considering the broad peaks of the amorphous particles, Fig. S4) and $\text{^{13}C}$ NMR spectra (Fig. S3). Therefore, the local order of the silica zeolite framework as well as the OSDA conformation and positioning in this framework do not present any significant variations with grinding that will otherwise modify the spectra. This is different from what is observed by $\text{^{29}Si}$ NMR when varying the thermal duration with a fixed grinding time (vide infra).

3.2. Thermal treatment duration

The duration of the thermal treatment is another key parameter that we have investigated while keeping other parameters constant (grinding time of 15 min, using silica gel and fixed composition). The XRD patterns of the samples synthesized with less than 3 h of thermal treatment show scattering related to the amorphous silica (Fig. S5). With further increasing of the thermal treatment, Bragg peaks of the $\text{Pnma}$ orthorhombic phase characteristic to Silicalite-1 start appearing. As the amplitude of such characteristic peaks increases with time, the scattering related to the amorphous particles decreases (Fig. S5 and Fig. S6). No other peaks related to impurities or a secondary phase are detected.

The crystallization of the sample was detected as early as 3 h in accordance with the results of F. Xiao and coworkers [13] and pure crystals were obtained within 13 h at 448 K. The evolution of the material can be divided into three main stages (Fig. 3). Stage I is the induction period during which only the amorphous silica exists, happening in periods less than 3 h (~the first 90 min). Within 3 h, the crystallinity percentage of the sample reaches ca. 9% indicating the
beginning of formation of the zeolitic crystals (stage II). At this stage (crystallization/crystal growth), amorphous and crystal particles coexist up to the point where the sample is fully crystalline ($10h < t ≤ 13h$) which is the beginning of the aging (stage III).

We were able to characterize the crystallization of the SF MFI zeolites by acquiring SEM images of samples synthesized with different thermal treatment durations. Within the first induction stage, we observe the beginning of the particles’ arrangement in comparison with the amorphous precursor without thermal treatment (Fig. S7). At this stage, the particles seem to start aggregating to form the crystals in the next stage (Fig. 4). After 3 h of thermal treatment
(crystallization stage), we observe the first formed crystals growing out of the amorphous feed (crystallization of amorphous particles) (Fig. 4 and Fig. S8). In this case, the crystal growth keeps proceeding in an intergrown manner with the increase of the thermal treatment. At 13 h of thermal treatment no amorphous-like particles can be observed which agrees with the formation of a pure crystalline sample deduced from PXRD pattern (Fig. 3 and Fig. S6b).

The crystals at 13 h are highly twinned and their measured size is smaller than the measured for the initial crystals (Fig. S9 and Fig. 4). The reason is that at this stage the mother crystals are covered with the newly formed smaller ones which gives a smaller apparent size (since only the smaller crystals are observable). Interestingly, during the third stage (aging) the crystals appear less intergrown and more separated (Fig. 4 and Fig. S10). The secondary grown crystals are bigger in this stage. Changes in SF crystal sizes with the thermal treatment duration has also been reported in literature [15]. The fact that the crystals get further separated and their sizes change with time suggests that a chemical rearrangement mechanism takes place in the growth of zeolites using the SF method.

![Fig. 4. SEM images of SF silicalite-1 samples synthesized with 15 min initial grinding and thermal treatment at 448 K for different periods.](image-url)
The samples synthesized with different thermal treatment durations were also investigated using TGA. The experimental/theoretical % (wt./wt.) weight loss ratios keep increasing with the thermal treatment duration, as in the case of crystallinity, until they are finally matching the theoretical value at 13 h that corresponds to a fully crystalline sample (Fig. 3). A similar evolution profile was also obtained for the F/Si ratio using EDX analyses (Fig. S11). Therefore, we conclude that the amorphous silica does not incorporate the OSDA and that the incorporation of the OSDA into the silica is related to the formation of the crystalline MFI framework. This conclusion is also confirmed with the $^{13}$C NMR results (vide infra).

$^{13}$C NMR CP-MAS spectra recorded under the same conditions show typical peaks of TPA hosted by the Silicalite-1 zeolite [22] for the samples synthesized with the SF method (Fig. 5). The relative intensity of the $^{13}$C peaks keep increasing with the thermal treatment duration in agreement with the progressive incorporation of the OSDA with the thermal treatment previously deduced from PXRD and TGA data. The double peak located between 60 and 70 ppm corresponds to the carbon bound to the nitrogen ($C_\alpha$). The composite peak in the middle is assigned to the C in the middle of the propyl chain ($C_\beta$). The last carbon at the end of the chain ($C_\gamma$) gives rise to the double peak located at ca. 10 and 12 ppm [22]. The peak around 10 ppm is assigned to the methyl groups inside the zigzag channels, while the peak around 12 ppm corresponds to the ones inside the straight channels [23]. It is worth noting that these peaks start to be clearly visible at 3 h, and that the characteristic splitting of $C_\gamma$ is not visible below 3 h (Fig. S12). From previously presented XRD and SEM data, 3 h is the period during which first crystals start forming. The sample synthesized with 1.5 h thermal treatment show very low $^{13}$C peaks that could be due to remaining TPA$^+$ salt impurities not completely removed by the washing step which was also the case with the sample with no thermal treatment (Fig. S12). This demonstrates again that no other $^{13}$C peaks that could correspond to TPA inside an amorphous silica particle can be detected. The impurity peaks presenting only in the sample synthesized
with longest period (28 d) are related to the degradation of the excess OSDA which is also observed by the color difference in the obtained powder (Fig. S13).

![Normalized plots

Fig. 5. $^{13}$C$^{[1]}$H CP-MAS spectra of TPA hosted by Silicalite-1 zeolites synthesized with the SF method at 448 K with different thermal treatment durations and 15 min of initial grinding ($\nu_0^{[13]C} = 75.5$ MHz, $\nu_{\text{MAS}} = 5$ kHz). Peaks assigned with * are related to degradation impurities of the excess OSDA.
Since the samples were synthesized in F-media, it was also worth inspecting them with $^{19}$F NMR. The recorded $^{19}$F NMR spectra are presented in Fig. 6. At the point when the crystallization starts (at 3 h), a peak located at ca. -63 ppm appears corresponding to fluorine in the \([4^15^26^1]\) cages of the silicalite-1 [21,24]. The two peaks detected in the range between -120 ppm and -140 ppm can be assigned to extra framework fluoride salts [21,25]. The presence of SiF$_6^{2-}$ related to the peak at ca. 127 ppm was also reported by Wu et al. [13] but in our case these ions are present in low quantities based on the signal intensity. The small peak at ca. -78 ppm was previously assigned to fluorine in defective sites [21,26]. With increasing the thermal treatment, the signal of the peak at ca. -63 ppm increases indicating the progression in incorporating fluorine atoms in the cages of silicalite-1 crystals.

![Fig. 6. $^{19}$F MAS NMR spectra for SF samples synthesized with different thermal treatment durations and 15 min of initial grinding ($\nu_0[^{19}F] = 564.7$ MHz, $\nu_{\text{MAS}} = 20$ kHz). Peaks assigned with (*) corresponds to spinning side bands.](image)

$^{29}$Si CP-MAS NMR can provide additional information on the nature of the species formed and on the local geometrical order. During the induction period, the spectra show only two broad peaks (Fig. S14). The peak located at ca. 100 ppm is related to the Si atoms bonded to three O-Si bridges ($Q^3$) in connectivity defects (silanol sites) of the zeolite or in other amorphous silica
species. The case here is the latter, since only the amorphous particles are present at this stage.

On the other hand, the chemical shift range of the other peak corresponds to Si atoms bonded to four O-Si bridges (Q$^4$). Its width is also consistent with the presence of amorphous silica species. At the beginning of the crystallization stage (3 h), the Q$^4$ peaks related to the resonances of the 12 Si sites of the Pnma phase start to appear overlapped with the Q$^4$ peak of the amorphous particles (Fig. S14).

From Fig. 7, we observe the evolution of the $^{29}$Si peaks after the induction period. The Q$^3$ peak keeps decreasing with increasing the thermal treatment duration. When the crystallization is fulfilled, it is no more observed. This indicates the absence of amorphous particles as observed by XRD and SEM (Fig. S6 and Fig. 4) and also silanol defects in the zeolite. The last broad peak located at ca. -125 ppm is an exchange peak [27] linked to the rapid jumps of F atoms between two Si locations inside the [4$^1$5$^2$6$^2$] cages changing the Si coordination between four and five.

Fig. 7. $^{29}$Si CP-MAS NMR spectra ($v_0$[$^{29}$Si] = 79.5 MHz, $v$MAS = 5 kHz) of a series of SF silicalite-1 samples synthesized at 448 K for 6 h, 9 h, 13 h, 40 h, 5 d, 10 d, and 28 d. The initial precursors were ground for 15 min prior to the thermal treatment.

It is noteworthy that the listed $^{13}$C NMR spectra in Fig. 5 didn’t show a clear progressive trend in terms of lineshape changes with the thermal treatment duration. The peak width and the
relaxation time provide insights into the evolution with the thermal treatment. This is shown by plotting the effective transverse relaxation time $T_2^*$ related to the FWHM as a function of the thermal treatment duration for three different peaks: two corresponding to the $C_\alpha$ and one to the $C_\gamma$ of the straight channels (Fig. 8a). This probably means that once the OSDA is incorporated in the silica MFI framework, it immediately takes its final and specific conformation [28,29], and that only slight changes may occur in its environment with extending the thermal treatment.

The case is different for $^{19}$F NMR spectra. The width of the peak at -63 ppm decreases with the increase of the thermal treatment duration (Fig. S15) along with a very slight change in the chemical shift position (~ 0.1 ppm). The thermal treatment influences the fluorine environment inside the crystals most probably due to a distribution decrease of the F atoms present in non-defective sites [21]. This increase in local order deduced from the increase in $T_2^*$ is shown in Fig. 8b.

We also observe a continuous decrease in the width of the $^{29}$Si Q$^4$ peaks of the zeolites even after reaching the fully crystalline state (beyond 13 h) (Fig. 7). This is shown by plotting $T_2^*$ as a function of the duration time (Fig. 8c) for two nonoverlapping peaks at -109.7 and -117.5 ppm corresponding to $T_8$ and $T_9$ sites respectively (see Fig. S16 for Si sites numbering). Measurements of the spin-echo transverse relaxation times $T_2'$ also show an increase with the thermal treatment (Table S1). The increase in both $T_2^*$ and $T_2'$ points to the progressive decrease in defects in the zeolite structure. This adds to our conclusion that an evolution, both in morphology and local order, occurs even after reaching the fully crystalline state. Changes in the peaks’ width weren’t observed when varying the grinding time (Fig. S3). Therefore, the local order is increased by solely prolonging the thermal treatment duration. A general conclusion on the effect of the thermal treatment duration is also included in section 3.4.
Fig. 8. The effective transverse relaxation time ($T_2^*$) as a function of thermal treatment duration for: a) three different peaks of $^{13}$C spectra at 65.6 and 62.7 ppm corresponding to Cα and at 11.5 ppm corresponding to Cγ in straight channels, b) peak at ca. 62.9 ppm of $^{19}$F spectra corresponding to F in the [415262] cages, c) two peaks of $^{29}$Si spectra at -109.7 and -117 ppm corresponding to T8 and T9 sites respectively.

3.3. Role of water

The role of water can be inferred first by comparing the SF method with the conventional hydrothermal method. We chose to conduct this comparison sticking to the F- route for both (yielding higher local order in the crystals [30]) and using conditions that ensure a full crystallinity and with identical molar ratios (except for water). For long thermal durations, there are no big differences observed in size and morphology for the two methods (Fig. S17a-b). When comparing their $^{29}$Si spectra (Fig. S17c), we see that the HT one is more locally ordered (narrower $^{29}$Si peaks) even though the thermal treatment duration for the SF (synthesized with silica gel) was doubled (28 d). In a recent study [29], we have discussed the local disorder attributed with
the SF method and compared it with the HT method. We concluded that the disorder here is statistical, not correlated, and probably due to a more defective crystallization. When using fumed silica with the SF method, the local order as seen by NMR (FWHM) was greatly enhanced but still not fully reaching that of the HT one (Fig. S17c). This local disorder in comparison with the HT sample was also observed on their $^{19}$F spectra (Fig. S18). The FWHM of the $^{19}$F peak was reduced by 39% when using the HT synthesis. The difference was reduced to ca. 5% when fumed silica was used as the Si source for the SF synthesis (Fig. S18). $^{13}$C NMR results show similar spectra for both samples (Fig. S19). In the case of HT synthesis, water is used as a solvent whereas in the SF method water quantity is scarce to cause any dissolution. Since the two methods have differences in their reacting phases, they possess different diffusion and reaction mechanisms which can explain any differences observed.

Fig. 9. a) 1D $^{17}$O MAS NMR spectra ($v_0$ [$^{17}$O] = 81.4 MHz, $v_{MAS}$ = 18 kHz, 0.5 s recycling delay, 1024 total scans) of Silicalite-1 as-synthesized sample with the SF method. b) Its recorded and sheared 2D $^{17}$O MQMAS spectrum ($v_0$ [$^{17}$O] = 81.4 MHz, $v_{MAS}$ = 18 kHz).

The role of water has been considered as a catalyst [12,31] in the SF synthesis of zeolites. As a further step to verify the role of water, we decided to carry out the synthesis using $^{17}$O labelled water (Fig. S20). $^{17}$O is the only NMR active nucleus for oxygen with a very low natural abundance (~0.037%). The $^{17}$O NMR signal from the SF sample synthesized with labelled water
(and no grinding) was detectable with one single scan, a condition that precludes any observation for $^{17}$O naturally abundant zeolites. We could actually record an intense 1D spectrum within minutes and a 2D MQMAS one within hours at 14.1 T (Fig. 9). These $^{17}$O spectra are similar to those previously observed for other $^{17}$O silica phases and correspond to Si-O bonds [32–34]. Besides a more complete $^{17}$O study that is currently ongoing, we conclude that the silica framework of the SF sample has been highly enriched in $^{17}$O using labelled water. This result reveals that water participates in the formation of the siloxane bonds through hydrolysis and condensation equilibrated reactions (Eq. 1). This favors the rearrangement of the silica network and the formation of the zeolite framework, thanks to the presence of silanol groups. It also explains the observed failure of the synthesis when water is completely absent (and using dried precursors) (Fig. S21). Therefore, a minimal amount of water is essential here for the synthesis. Additionally, our straightforward labelling method without preliminary grinding proves to be effective in yielding highly $^{17}$O enriched zeolites.

\[
\begin{align*}
\text{hydrolysis} & \quad \text{condensation} \\
\text{SiOSi} + H_2O^* & \quad SiOH + HO^*Si \\
\text{condensation} & \quad \text{hydrolysis} \\
& \quad SiO^*Si + H_2O \\
\end{align*}
\]

$$\text{Eq. 1}$$

3.4. New insights in the SF formation mechanism

Based on the results presented in the previous sections, we can visualize the journey of the formation of zeolites with the SF method. At first, reactants in the powder require the presence of water either by using non-dried precursor or by adding small quantity of water (molar ratio Si/H$_2$O =1 in our case) that would not dissolve the powder. In the absolute absence of water, the product is amorphous which agrees with some previous reports [7,14,35]. When $^{17}$O labelled water was used in the synthesis, the final formed zeolite framework was enriched with $^{17}$O. This highlights the important role of water in zeolite syntheses participating in Si-O bonds formation within the SF synthesis.

The grinding step only assists in accelerating the crystallization, but fully crystalline samples can also be obtained without any grinding (Fig. 2). Nada et al. [16] reported obtaining quartz when
performing the synthesis without any grinding/milling, but the used reactants were different. Additionally, the grinding duration of the reactants decreases the obtained crystal sizes but has no effect on the nanoscale order of the silica framework. The reason behind this could be linked to the decrease in size of the precursors as well as to the increase in nucleation rate through a more homogeneous distribution of reactants.

During the thermal treatment, the particles start to aggregate forming new particles, within the first hour in the frame of our experimental conditions, initiating the crystallization observed after three hours. The crystals grow feeding from the amorphous particles via solid phase transformation [7]. This growth mechanism is also shared with the HT synthesis where both solid-phase and solution mediated growth mechanisms coexist [2,36]. Herein, we also observe a direct incorporation of the OSDA inside the zeolite framework without the formation of an intermediate OSDA-silica assembly. Cundy and Cox [2] described the presence of OSDA bound in amorphous precursor complexes to be in accord with the solution-mediated growth mechanism. This is not the case for the solid phase transformation occurring here.

Changes keep taking place even after full crystallization. Local rearrangement and growth in crystal sizes are observed. The change in the crystal sizes with the absence of the amorphous precursors (since only crystals are present) indicates that the crystals can rearrange with prolonging the thermal treatment. We have also shown ($^{19}$F, $^{29}$Si NMR) that the local order of the zeolite framework keeps increasing with the thermal duration, although TPA molecules adopt a well-defined configuration since “the beginning” ($^{13}$C NMR). Therefore, the chemical transformation and crystal rearrangement concern the reordering of the siloxane shell around TPA. All these evolutions are made possible by the continuation of hydrolysis and condensation reactions (Eq. 1).
4. Conclusion

In this study, we determine the actual role of grinding in the solvent-free synthesis of zeolites. We show that grinding only helps in accelerating the crystallization and that a completely grinding-free SF synthesis can be carried out. Besides that, we conclude that the grinding duration influences the final size of the formed crystals. Careful studies of the crystallization under solvent-free conditions indicate that the crystals are formed once the OSDA is incorporated, and no other hybrid OSDA-intermediate species are found. Also, prolonging the thermal treatment duration affects the morphology and the local order in the crystals investigated by multinuclear NMR experiments. We determine the role of water in the synthesis participating in forming T-O-T bonds in the framework of MFI zeolites. We also propose a facile $^{17}\text{O}$ labelling method for zeolites, allowing high enrichment levels to be reached (potentially reaching $\sim 13\%$ $^{17}\text{O}$ here, when starting from 40% labeled water).

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References


