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On the hydrothermal stability of MCM-41. Evidence of capillary tension-induced effects

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ABSTRACT

MCM-41's limited hydrothermal stability has been often related to the hydrolysis of Si–O–Si bonds due to the low degree of condensation, its thin walls or a combination of them. In this work, evidence for an additional factor is provided; a physical effect that occurs during the drying of the hydrothermally treated calcined material due to the intense capillary stress exerted in water. Depending on both physical (i.e. mechanical) and chemical (i.e. hydrolysis) resistances, the structure undergoes differently. Three MCM-41 samples with different degree of condensation were investigated. The most remarkable results are found with un-aged TEOS based material, which gets fully disordered and shrunk for all applied hydrothermal temperatures in water. Comparison between water and a low-surface-tension-solvent drying revealed that capillarity is responsible for the loss of ordering (and shrinkage) at moderate hydrothermal temperatures. The material's structure is hexagonal and shrinkage-free under the low-surface-tension-solvent route. At a high hydrothermal temperature, hydrolysis is extensive and responsible for the loss of ordering. The other remarkable finding regards the aged MCM-41 meso-structure that maintains the hexagonal features at all applied temperatures in water, and it is more stable against capillarity at high temperature. The Na-metasilicate based material is mechanically very stable and gets disordered at high temperature due to hydrolysis.

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1. Introduction

The mesostructured MCM-41 material has drawn significant interest in various fields due to its high ordering and surface area. The pore size, and therefore the surface area and pore volume, can be adjusted using various types of alkylammonium based surfactants, typically ranging from C₈ up to C₁₈ of the main alkyl chain [1–3]; features that are consistent with the work of Yanagisawa et al. on equivalent mesoporous silica networks [4]. Many uses have been reported for MCM-41 including catalysis, adsorption, separation, sensing, optics, electronics and drug delivery [5–14]; more recently biomass-based applications have been documented [15–18].

The limited hydrothermal stability is considered one of MCM-41's weaknesses, meaning thermal treatments in water or steam, or

both. This was reported by Kim and Ryoo [19]. They reported that MCM-41, and MCM-48, disintegrate in water at temperatures above 343 K; the disappearance of the ordered features was ascribed to hydrolysis and collapse of the structure due to the ill-crystallized thin walls. The effect was found to be irreversible and was even observed at room temperature in wet saturated atmospheres [20,21]. Cassiers et al. [22] reported a systematic study on various types of relevant ordered mesoporous materials under steam; it was found that MCM-41 is the less stable structure under the applied conditions; 30 vol.% H₂O at 400 °C for 48 and 120 h.

Research in this area has been mostly dedicated to improve the hydrothermal stability of MCM-41 in two directions; synthetic or post-synthetic routes. On the synthetic approaches, the application of hydrothermal restructuring conditions, meaning water rather than the synthesis mother liquid, was found to enhance the stability significantly. Sayari et al. [23] and Kruk et al. [24] made use of water-based post-synthesis treatment at 413–423 K from 5 h to 19 days. Redispersing the as-synthesized dried material in water at 333 K for 24 h was also beneficial for nano-sized MCM-41 [25];

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though the surface area decreased considerably upon this treatment. Its adsorption capacity increased due to the more pronounced hydrophobic nature of the surface. Landau et al. [26] observed a similar beneficial effect by ageing the gel at 373 K for 144 h. Ribeiro Carrott et al. found out that a hydrothermally synthesized material was somewhat more stable than the room-temperature synthesized counterpart [27]. Mokaya claimed favourable conditions (423 K for 96 h [28] up to 196 h [29] in the mother liquid) to have a positive impact on the material's hydrothermal stability, either under steam or boiling water. A two-step gel crystallization was proposed by Mori et al. [30] involving 3 days at 308 K and an additional 3 days at 413 K. The so-derived MCM-41 exhibits excellent resistance to water; surviving in boiling water for more than a week. A post-treatment at 403 K for 24 h in the mother liquid was beneficial for silica foams [31].

Salt addition effects have also played a positive role in enhancing the hydrothermal stability of MCM-41. Researchers describe salt-based strategies that modify the crystallization process, such as NaCl [26,32–36], KCl [32], Na-acetate [32,33], EDTANa₄ [32,33,35], ADANa₂ [33], NaNO₃ [33,36], tetraalkylammonium [37], NaBr [37], NaF [38,39] and Na₂SO₄ [36]. The anions, counteracting the cationic surfactant, have been found to be relevant as well in the post-synthesis hydrothermal treatment of MCM-41 [40].

Hydrophobization of the MCM-41's surface has been an effective mean to increase its hydrothermal stability; the material resembles a hybrid structure such as the organo-silicas that have proven to have superior hydrothermal stability [41,42]. Approaches on MCM-41 include liquid-phase silylation with mono- and methylchlorosilanes [2,43,44], co-condensation of tetraethylorthosilicate with different organic silanes [45], intercalation of silanes by ion imprinting method [46]. A very straightforward approach has been recently proposed for silicas and aluminas [47], consisting of the deposition of a thin film of a sugar-derived carbon.

The addition of aluminium into the MCM-41 structure or onto the surface enhances the hydrothermal stability. Chen et al. [48] reported that the Al-containing MCM-41 is more stable towards treatments in pure distilled water at 298–373 K for 4 h. Mokaya described various post-synthetic alumination routes, such as the aqueous aluminium chlorohydrate treatment [49] and impregnations aided by supercritical fluids (CO₂ and propane) [50]; the same group reported a route via the mixed-gel synthesis [51], and a slightly more complex protocol including ageing [52]. For all of these routes an increased hydrothermal stability was found. Shen and Kawi [53,54] rationalized the effect of the Si/Al ratio with the fact that defects always accompany materials with high Al content; they concluded that post-synthesis alumination is the most effective way to have good hydrothermal stability without any structural defects. Li et al. corroborated that Al is effective in pure steam at temperatures as high as 800 °C [55].

Adjustments of the pH have also been reported; an acid titration during ageing improves the long-range ordering as well as the hydrothermal stability [56]; combined routes consisting of pH-based adjustment with salt additions have been effective as well [26,32,38].

Seed crystallization gives rise to more robust structures. Nano-MCM-41 as a silica source was described by Mokaya et al. leading to high-quality hydrothermally stable MCM-41 [57]. Preformed zeolite nanoclusters have been successfully used for making highly hydrothermally stable mesoporous materials, based on nano-Silicalite-1 [58] and nanosized ZSM-5 [59]. Nanosphere-walled mesoporous silica, prepared from colloidal silica and citric acid as non-surfactant template [60], was found to be extraordinarily hydrothermally stable.

Finally, under an excess of tetraethylorthosilicate (high tetraethylorthosilicate to copolymer ratio) mesoporous structures with plugged pores were formed, with extraordinary hydrothermal stability [61].

The above-described methodologies clearly evidence a sustained effort into developing more robust mesoporous MCM-41 structures and mesoporous silicas in general. The structural disintegration of MCM-41 in water or steam has been ascribed to the rapid hydrolysis of relatively thin amorphous silica walls. Various factors have been identified to play a role, such as the wall thickness [22], polymerization degree [22], cross-linking density associated to the surfactant [62], role of entrapped framework sodium [63] that catalyzes the collapse of the structure. Lately the structural stability was correlated to the ratio of the amount of Si–OH to the pore wall thickness [21].

In this study, the role of the capillary tension during drying of the calcined materials that are hydrothermally treated has been investigated. This hypothesis is based on various ideas. First, in a recent study it was demonstrated that the capillary forces play a negative role after chemical detemplating a MCM-41 precursor via Fenton chemistry [64]; when the resulting material after Fenton detemplation is exchanged and dried in a low-surface tension solvent, the structure is well preserved, while drying in water results in structural damage associated to the capillary stress, due to the high surface tension of water. Secondly, procedures exist about solvent exchange before drying for processing gels [65–67], metal organic frameworks [68,69] and mesoporous germanates [70], which often result into collapse and shrinkage upon solvent removal. Here it is shown that the capillary tension associated to drying plays a role in the structural loss after the hydrothermal tests of calcined MCM-41. In particular, the most remarkable results are obtained for the un-aged MCM-41. Thus hydrolysis and capillary tension contribute to the hydrothermal damage, depending on the type of MCM-41 and the applied hydrothermal conditions.

2. Experimental

2.1. Synthesis

2.1.1. TEOS based MCM-41 material

The synthesis of this mesophase is based on the method reported by Grün et al. [71] using tetraethylorthosilicate (TEOS) and ammonia as catalyst without any hydrothermal stabilization. The organic template (cetyltrimethyl-ammonium bromide, CTAB) was dissolved in deionized milli-Q water and aqueous ammonia was added in the following amounts: 2.62 g CTAB, 122 g H₂O and 9.14 g aqueous ammonia (25 wt.%, Merck). This mixture was stirred (400 rpm) at 303 K. Around 10 g of TEOS (Si(OC₂H₅)₄, Aldrich) were added dropwise in ca. 0.5 h using a peristaltic pump (0.3 g/min). A gel with the following molar composition was formed: 1 TEOS: 0.152 CTABr: 2.8 NH₃: 141.2 H₂O. The material was recovered by filtration and washed with 500 mL of milli-Q water and dried overnight at 383 K. The calcination was carried out at 823 K for 5 h in a static-air box furnace at 1 K min^{−1} heating rate. The template-containing precursor was labelled as Tp while the calcined mesophase was named as Tc, where T denotes TEOS-based.

2.1.2. TEOS-based MCM-41 material with hydrothermal ageing

The synthesis of this mesophase is similar to the previous one in terms of gel composition and hydrolysis conditions. The difference comes from the applied post-hydrolysis hydrothermal treatment. The gel in the synthesis medium was transferred into a Teflon® bottle (BRAND®, Sigma–Aldrich) and this was heated at 378 K for 5 days under autogenous conditions. The material was recovered by filtration, washed with 500 mL of milli-Q water and dried overnight

at 383 K. The template-containing precursor was labelled as TAp while the calcined mesophase was named as TAc, where TA denotes TEOS aged.

2.1.3. Sodium metasilicate-based MCM-41 material

In this route the main differences are the Si precursor, which is Na-metasilicate, and the hydrothermal stabilization was carried out at 423 K (24 h) [72]. Sodium metasilicate (Na_2SiO_3 , 8.13 g) was added to 120 g of demineralized water and stirred for 30 min in a poly-propylene beaker. A second solution was prepared by mixing 4.84 g CTAB, 30 g milli-Q water and 10 g of EtOH (Lab Scan, *pro-analysis*) and stirred for 30 min. The two solutions were mixed and stirred for 30 min to obtain a clear gel. Afterwards, 15 g of 2.0 M H_2SO_4 (Merck) were added slowly within 10 min under vigorous stirring and the slurry was stirred at room temperature for 30 min. The beaker was covered with parafilm® to prevent evaporation. Another 15 g of 2.0 M H_2SO_4 were added at similar rate under vigorous stirring; the mixture was stirred during 1 h at room temperature. The so obtained gel, with composition 1 SiO_2 : 1 Na_2O : 0.2 CTAB: 143 H_2O : 0.9 H_2SO_4 , was transferred into a Teflon-lined steel autoclave and aged in the synthesis medium at 423 K for 24 h. After this period, the autoclave was quenched with cold water and the solid was recovered by filtration using 25 mL ethanol; the solid was washed four times with 10 mL of ethanol and three times with 200 mL of demineralized water. It was dried in air at 353 K overnight prior to calcination. The dried material was calcined at 813 K for 1 h in nitrogen flow of $50 \text{ cm}^3 \text{ min}^{-1}$ NTP with a heating rate of 2 K min^{-1} . The nitrogen flow was substituted by air and continued the calcination for 8 h at 813 K using a gas flow of $100 \text{ cm}^3 \text{ min}^{-1}$ NTP. The template-containing precursor was labelled as Mp while the calcined mesophase was named as Mc, where M comes from metasilicate.

2.2. Hydrothermal treatments

Around 250 mg of the calcined material were dispersed in 10 mL of water (Milli-Q) and heated to the corresponding test temperature (343, 358 or 373 K), and left for 5 h under gentle stirring. The experiments were carried out using test tubes ($\varnothing = 16 \text{ mm}$, $L = 100 \text{ mm}$). After the hydrothermal test, the excess water was removed by centrifugation at 4000 rpm and the wet material was dried in the test tube at 343 K overnight. Sample dissolution was quantified by weight difference. The resulting material was labelled with the suffix '(temperature.W)'; the temperature is given in degrees Kelvin and W means water-based drying.

2.3. Solvent exchange

In a separate protocol, the wet material after the hydrothermal treatment was washed and exchanged with *n*-butanol (Acros Organics, 99% extra pure) before drying; the aqueous slurry was centrifuged to remove excess water and washed by centrifugation four times with 5 mL of *n*-BuOH. Each washing step took ~15 min. The drying was carried out in two steps; overnight at 343 K and then the temperature was increased to 373 K and left for 5 h in order to remove the loosely adsorbed solvent residue. The resulting material was labelled with the suffix '(temperature.B)'; the temperature is given in degrees Kelvin and B means *n*-butanol-based drying.

Table S-1 summarizes the materials work-ups and used codes.

2.4. Characterization

Thermogravimetric analysis (TGA) was carried out with a Mettler-Toledo analyzer (TGA/SDTA851e) using a flow of synthetic

air of $100 \text{ cm}^3 \text{ min}^{-1}$ NTP. The samples were heated from 303 to 1173 K at 10 K min^{-1} to verify at which temperature the organic template is removed by calcination.

Small angle X-ray scattering (SAXS) measurements were carried out in a Bruker NanoStar instrument. A ceramic fine-focus X-ray tube, powered with a Kristallflex K760 generator at 35 kV and 40 mA, has been used in point focus mode. The primary X-ray flux is collimated using cross coupled Göbel mirrors and a pinhole of 0.1 mm in diameter providing a $\text{CuK}\alpha$ radiation beam with a full width at half-maximum of about 0.2 mm at the sample position. The sample-detector distance was 1.04 m. The scattering intensity was registered by a Hi-Star position-sensitive area detector (Siemens AXS) in the *q*-vector range of 0.1–2.0 nm. The accuracy of the SAXS measurements was estimated by the standard deviations (σ) of the main reflection (100) in the *q*-vector, accounting for the instrumental error, and intensity that takes into account the reproducibility in the sample preparation. Both parameters have low deviations, $\sigma = 0.6\%$ in the line position and $\sigma = 2.2\%$, for the intensity (Table S-2, Fig. S-1).

Nitrogen physisorption analyses (77 K) were carried out in a Micromeritics ASAP 2420. The samples were degassed in vacuum at 573 K for 10 h. The surface area was calculated using the standard BET method (S_{BET}). The single point pore volume (V_T) was estimated from the amount of gas adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distribution (PSD) was obtained from the BJH method using the adsorption branch of the isotherm; Φ_{BJH} represents the position of the maximum. The *t*-plot method was employed to quantify the micropore volume (V_μ).

^{29}Si solid state NMR spectra were recorded on a 300 MHz Agilent spectrometer operating at a field of 7.05T using a 9.5 mm pencil type MAS probe resonant at 59.596 MHz for silicon and 300.15 MHz for protons. A magic angle spinning at 4 kHz was employed. All spectra were recorded using spinal decoupling at 25 kHz rf-field strength (pulse duration 20 μs and 6° phase). Ramped cross polarization at a proton rf-field strength of 25 kHz and a 29 kHz rf-field on silicon was employed with 8 ms contact time. Chemical shifts were referenced with respect to tetramethylsilane. To ensure quantitative results, a Si T_1 measurement via cross polarization was recorded. The intensities of the Q_2 , Q_3 and Q_4 lines were obtained as a function of the recovery time by deconvoluting the series of spectra with the line parameters obtained by a good S/N CP-MAS spectrum. Typical T_1 values varied between 30 up to 712 s. These T_1 values were used to correct the intensities of the *Q*-species that were obtained in a direct polarization experiment with a waiting time of 900 s. The results have an estimated accuracy of 0.5%. The concentration of silanols relative to the total Si is calculated according to Igarashi et al. [21]:

$$\text{SiOH (mol\%)} = \left[\frac{2Q_2 + Q_3}{Q_2 + Q_3 + Q_4} \right] \times 100$$

A combined method (NMR with probe molecules-based FTIR) was proposed by Ide et al. [73], which distinguishes precisely accessible silanols from total bulk silanols; the observed deviation between total and accessible silanols for MCM-41 was relatively small, therefore we believe that the method proposed by Igarashi et al. [21] is acceptable for our interpretation, and allows relative comparison between the samples.

The electron microscopy measurements were performed using a TECNAI F30, operated at 300 kV, point resolution 1.9 nm, and Cs 1 mm, equipped with a $2\text{K} \times 2\text{K}$ Ultrascan CCD camera (Gatan).

3. Results

3.1. Calcined materials

The studied MCM-41 materials have different degrees of condensation in view of the applied hydrothermal ageing conditions. TEM pictures of the calcined mesophases (Fig. 1, top) reveal particle agglomeration (Tc) and larger aggregated particles (Mc and TAc). High resolution TEM (Fig. 1, bottom) and SAXS (Fig. 2) evidence a high structural ordering, characteristic of straight channels with $p6mm$ hexagonal symmetry. The three materials' synthesis routes employ the same surfactant (CTAB) to exclude any effect of surfactant's difference, in particular the possible effect of the decomposition products on the silica walls, which could affect the observed stabilities.

3.2. Hydrothermal stability of the calcined materials

The calcined MCM-41 mesophases were evaluated regarding the hydrothermal stability by treatments in liquid water at various temperatures ranging 343–373 K (Fig. 2).

SAXS analyses of hydrothermally-treated Mc material are shown in Fig. 2a. Changes in the structure are visible, with a reduction of the main 100-reflection and secondary ordering at all applied temperatures. The secondary reflections (Fig. 2a, inset) are maintained at 343 and 358 K, but nearly lost at 373 K. The material does not suffer from shrinkage, *i.e.* contraction of the unit cell, under hydrothermal conditions at any of the applied temperatures, as evidenced by the position of the 100 reflection, which is nearly equal to the calcined counterpart (Mc). Moderate material dissolution was found with a consistent increase with the hydrothermal temperature, 0.7, 1.6 and 3.9 wt.% (Table S-3).

Results for the hydrothermally aged TEOS-based MCM-41 material (TAc) are given in Fig. 2b. The SAXS intensity of the main reflection decreases significantly with the applied temperature; the secondary reflections vanish as well (Fig. 2b, inset). The structure

shrinks towards a smaller unit cell, as evidenced by the shift towards higher SAXS angles of both main and secondary reflections. The shrinkage appears to have an inverse relation with the applied hydrothermal temperature. Moderate sample dissolution was observed, ranging from 0.5 to 4.4 wt.% (Table S-3).

For the TEOS-based material (Tc), the main 100 reflection drops considerably with the applied temperature and nearly disappears at 373 K (Fig. 2c). The secondary SAXS features disappear already at 343 K (Fig. 2c, inset). These SAXS results are consistent with previous studies carried out in liquid water for a material combining TEOS/silica gel [19], water vapour at room temperature [21] and 40% steam at 400 °C [22] (the latter studies are based on purely TEOS-derived materials); which reported XRD disordering or textural reduction. The Tc material showed limited dissolution ranging from 0.1 to 2.9 wt.% (Table S-3). Quantification of the Si–OH groups (Fig. 3, Table S-4) shows that Tc(343.W) is hydrolyzed when compared to the bare Tc; it increases from 31.8 (Tc) up to 44.1% for Tc(343.W) while its drops to 27.6% for Tc(373.W). The obtained value at 373 K is 4.2% absolute units lower than that for Tc. This may be due to condensation reactions between adjacent surface Si–OH during drying or to the lower surface area ($735 \text{ m}^2 \text{ g}^{-1}$ compared to $1160 \text{ m}^2 \text{ g}^{-1}$ for the calcined material, Table 1) or both effects. A comparable condensation-related effect has been reported during the formation of xerogels [66].

3.3. Hydrothermal stability of the calcined materials considering low-surface tension-solvent drying

The hypothesis of this study supposes that the material is hydrolyzed during the hydrothermal treatment; the hydrolyzed surface is exposed to intense capillary forces during drying in the cylindrical pores that are able to shrink the structure when this is not mechanically rigid. Hence the collapse may not only be associated to hydrolysis, but also to the fact that water has a relatively high surface tension. Calculation of the capillary pressure by the Young–Laplace equation [74] for the Tc material, as example,

Fig. 1. TEM (top) and high-resolution TEM (bottom) of the calcined MCM-41 mesoporous materials based on: a) TEOS, b) TEOS aged and c) Na-metasilicate.

Fig. 2. SAXS patterns for the MCM-41 based materials after hydrothermal conditions at 343, 358 and 373 K. Mesophases and calcined materials are included for comparison. Insets: secondary 110 and 200 reflections, following the same sample order than in the main graphs. Sample codes and treatments are summarized in Table S-1. Dot lines correspond to the 100 reflection of the template-containing precursors.

having cylindrical pores of 2.7 nm, assuming a contact angle between water and silica of 45° and pure water ($\gamma = 71.95 \text{ mN m}^{-1}$) [75] reveals that the adhesion pressure within the walls is 745 atm. Such a pressure can mechanically deform the structure when the material is not stable enough. A way to reduce the capillary stress could be replacing water by a low-surface-tension solvent and drying the wet solid in that solvent. The solvent must fulfil another requirement; having a higher boiling point than water, in order to evaporate water preferentially before the mesoscopic menisci are formed. If the boiling point would be lower than water, the pores can get enriched in water during the evaporation and the capillary

Fig. 3. Solid state ^{29}Si MAS NMR spectra of relevant TEOS-based materials after various treatments. Quantification is provided in Table S-4. a) Tc(343.B), b) Tc(373.W), c) Tc(343.W) and d) Tc.

Table 1

Textural properties (N_2 at 77 K) of Tc based MCM-41 materials after hydrothermal stability tests in water or after *n*-BuOH exchange.

Material	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{T} ($\text{cm}^3 \text{g}^{-1}$)	Φ_{BHT} (nm)
Tc	1160	0.858	2.7
Tc(343.W)	1026	0.549	2.1
Tc(343.B)	1100	0.613	2.1
Tc(358.W)	809	0.427	Broad, max. < 2.0
Tc(358.B)	1168	0.632	2.1
Tc(373.W)	735	0.649	Broad
Tc(373.B)	797	0.545	Broad

forces will eventually rise. These conditions are fulfilled by *n*-BuOH [64]; the boiling point is +18 K higher than water while the surface tension is ~0.4 times lower than water (in terms of pressure, ~260 atm for similar conditions given before).

Related work about drying gels in low surface tension solvents uses *N,N*-dimethylformamide (DMF) for reducing the cracking of sol–gel monoliths [76] or liquid CO_2 , ethanol, acetone, dioxane, acetonitrile, among others [66]. DMF has +53 K difference in boiling point compared to water but the surface tension is higher than *n*-BuOH with a factor 1.4 (Table S-5).

3.3.1. Structural properties of the derived materials

The effect of the *n*-BuOH exchange on the metasilicate-based material was not significant (Fig. 4). The main reflections, and secondary ones when present, were slightly more intense (B samples) at the three studied hydrothermal temperatures, when

Fig. 4. Effect of the *n*-BuOH exchange on the structural ordering for the Na-metasilicate-based MCM-41 materials after aqueous hydrothermal conditions at (a) 343, (b) 358 and (c) 373 K. Calcined and mesophase are included for comparison. Insets: secondary 110 and 200 reflections, following the same sample order than in the main graphs. Dot line corresponds to the 100 reflection of the template-containing precursor (Mp).

compared to the directly water-dried counterparts (W samples). At 373 K the secondary reflections are not improved after *n*-BuOH exchange (Fig. 4c, inset). The structure is fully converted from hexagonal into a wormhole structure, either in water or in *n*-BuOH at 373 K.

The effect of solvent exchange on the TEOS-based hydrothermally treated material is more pronounced (Fig. 5); shrinkage is not present at 343 and 358 K treatment while the water-dried counterparts shrink, even more than the calcined case (Fig. 5a and b). Shrinkage is present at 373 K but it is only slightly smaller than the water-dried counterpart (Fig. 5c); the latter compensates shrinkage with the applied hydrothermal temperature as discussed earlier. Remarkably, the intensity of the main and secondary reflections are notably enhanced when *n*-BuOH exchange is applied. These comparative results with water indicate that the low capillary tension in *n*-BuOH plays a positive role in preserving the structure during drying.

Remarkable improvements were observed for the calcined unaged TEOS based material. Less shrinkage is found and the intensity of the 100 reflection is much more intense when compared

Fig. 5. Effect of the *n*-BuOH exchange on the structural ordering for the TEOS-aged MCM-41 materials after aqueous hydrothermal conditions at (a) 343, (b) 358 and (c) 373 K. Calcined and mesophase are included for comparison. Insets: secondary 110 and 200 reflections, following the same sample order than in the main graphs. Dot line corresponds to the 100 reflection of the template-containing precursor (TAp).

to the water-dried counterparts (Fig. 6). The secondary reflections are detected at 343 and 358 K, for the materials Tc(343.B) and Tc(358.B), while those reflections are absent in water (Fig. 6a and b, insets). At 373 K the secondary reflections are not observed neither in water nor *n*-BuOH (Fig. 6c, inset), meaning that the structure is converted from hexagonal into wormhole.

3.3.2. Textural properties of the derived materials

The un-aged TEOS-based materials were further studied by gas adsorption since they showed the most remarkable SAXS-based results in terms of structural preservation. The N₂ gas adsorption isotherms are shown in Fig. 7 and the derived textural parameters are given in Table 1. The calcined Tc sample shows the typical reversible isotherm characteristic of MCM-41, with a sharp capillary condensation at around 0.2–0.3 in the relative pressure (*p*/*p*₀). This corresponds to a relatively sharp pore size distribution centred at 2.7 nm in the BJH plot (Fig. 7a, right). No microporosity was detected. The BET surface area and pore volume account 1160 m² g^{−1} and 0.858 cm³ g^{−1}.

Fig. 6. Effect of the *n*-BuOH exchange on the structural ordering for the TEOS-based MCM-41 materials after aqueous hydrothermal conditions at (a) 343, (b) 358 and (c) 373 K. Calcined and mesophase are included for comparison. Insets: secondary 110 and 200 reflections, following the same sample order than in the main graphs. Dot line corresponds to the 100 reflection of the template-containing precursor (Tp).

Treatment in water at 343 K, Tc(343.W) gives a reduction of the capillary condensation at 0.2 p/po (Fig. 7a, left) that corresponds to a much flatter pore size distribution (Fig. 7a, right). Consequently the pore volume drops to $0.549 \text{ cm}^3 \text{ g}^{-1}$. The BET surface area remains relatively high with $1026 \text{ m}^2 \text{ g}^{-1}$ because the pores are smaller (2.1 nm) due to the shrinkage. The *n*-BuOH-exchanged material, Tc(343.B), has a steeper capillary condensation and a more defined (*i.e.* more intense) pore size distribution, centred at 2.1 nm. The surface area and pore volume of this material increases when compared to the water-dried counterpart, with $1100 \text{ m}^2 \text{ g}^{-1}$ and $0.613 \text{ cm}^3 \text{ g}^{-1}$. These results are in line with the better structural preservation revealed by SAXS when *n*-BuOH was applied, that showed the presence of the secondary reflections (Fig. 6a).

Concerning the 358 K treated samples (Fig. 7b), the typical MCM-41 isotherm shape is lost when the material is dried in water; the pore size distribution is much broader than the 343 K-water-treated material. The surface area and pore volume drops considerably to $809 \text{ m}^2 \text{ g}^{-1}$ and $0.427 \text{ cm}^3 \text{ g}^{-1}$ due to the severe structural collapse as discussed in Fig. 6b. When *n*-BuOH exchange is applied

the textural features are better preserved; the isotherm maintains the capillary condensation and consequently the pore size distribution is relatively narrow (Fig. 7b, right). The derived textural parameters of this material, Tc(358.B), are relatively high with $1168 \text{ m}^2 \text{ g}^{-1}$ and $0.632 \text{ cm}^3 \text{ g}^{-1}$, compared to the calcined material. The high surface area is due to the smaller pores, centred at 2.1 nm that contribute less to the pore volume but more to the surface area.

At 373 K, the isotherms show for both cases (water or *n*-BuOH) no capillary rise at 0.2 p/po and desorption hysteresis with a closure point at around 0.45 p/po (Fig. 7c, left). This is an indication of pores with wide parts and restrictions. There is no evidence of well-defined mesoporosity in the adsorption pore size distributions (Fig. 7c, right). The surface areas are the lowest (735 and $797 \text{ m}^2 \text{ g}^{-1}$) and the pore volumes are relatively low, 0.649 and $0.545 \text{ cm}^3 \text{ g}^{-1}$.

The textural characteristics corroborate the observations on the structural changes: intense pore size distributions and high textural parameters together with defined SAXS secondary reflections are found, when *n*-BuOH exchange is applied for hydrothermal temperatures below 373 K. At 373 K the hydrolysis leads to a pronounced and irreversible damage.

The SiOH concentration for the Tc(343.B) material was estimated at 41.8% (Table S-4) that is comparable to the water-dried counterpart, 44.1% for Tc(343.W), revealing that the surface is indeed hydrolyzed. When combining NMR, SAXS and textural analyses, it is concluded that the *n*-BuOH-exchanged Tc(343.B) sample is nearly equally hydrolyzed but it is structurally better preserved because of the lower capillary tension that the material has been subjected to.

4. Discussion

The obtained observations have been summarized in Fig. 8, which comprises water and *n*-BuOH drying conditions for the three materials at three hydrothermal temperatures. This mapping visualizes changes in ordering and shrinkage upon treatments. It is generally observed that *n*-BuOH drying prevents shrinkage for the Tc and TAc mesostructures.

The Na-metasilicate mesostructure (Mc) is mechanically stable since it does not show structural shrinkage under all conditions in water. The structure remains hexagonal up to 373 K, where it is converted into wormhole. Therefore, this mesostructure suffers from hydrolysis at 373 K, which explains the ordering loss, but it is mechanically stable in terms of capillary stress. Possible reasons for this behaviour can be the role of exchanged CTA^+ with Na^+ , or the relatively high applied hydrothermal temperature, 423 K, compared to the other materials' conditions, or both effects.

The hydrothermally aged TEOS-based MCM-41 material (TAc) has a more complex hydrothermal stability. The hexagonal ordering is preserved in water at all applied temperatures, but it shrinks due to capillarity in water. This is overcome by applying *n*-BuOH where the unit cell is preserved as well as the hexagonal ordering. Shrinkage in water has an inverse relation with the applied hydrothermal temperature. This can be explained by the possible stabilization of the structure during the hydrothermal tests itself becoming more stable against mechanical stress. This structure seems to be very stable towards hydrolysis and capillarity at high temperature which is remarkable. Former studies claimed that fumed silica-derived syntheses give rise to the most stable MCM-41 [21,22].

The TEOS-based material (Tc) revealed the lowest hydrothermal stability, in terms of hydrolysis and capillarity, when dried in water. Severe shrinkage and loss of hexagonal ordering was found at all temperatures. Shrinkage was progressive with the applied hydrothermal temperature. Remarkably, both ordering and unit cell

Fig. 7. Nitrogen adsorption isotherms (left) and BJH pore size distributions (right) for the TEOS-based MCM-41 materials after aqueous hydrothermal conditions, dried in water or after *n*-BuOH exchange: a) 343; b) 358 and c) 373 K (hydrothermal temperature). The calcined material is included for comparison.

Material	H ₂ O			<i>n</i> -BuOH		
	343 K	358 K	373 K	343 K	358 K	373 K
Mc						
TAc						
Tc						

Fig. 8. Effect of the different drying media (H₂O, *n*-BuOH) after the hydrothermal conditions (343–373 K) for the three studied materials. For simplicity, a single particle has been plotted in order to highlight shrinkage.

Fig. 9. Suggested solvent-based pathways upon hydrothermal treatment at 343–358 K for less stable MCM-41 material (Tc). A) Route in water where capillary stress gives rise to a disordered and collapsed structure. B) Low-surface-tension route, after *n*-BuOH exchange where capillary stress is reduced and order/unit cell are preserved. For simplicity, a single particle has been plotted. The indicated capillary pressures are calculated assuming a contact angle of 45° and cylindrical pores of 2.7 nm. Surface tensions can be found elsewhere [75].

dimension are preserved when applying the *n*-BuOH route for materials treated at temperatures of 343–358 K; comparison between water and *n*-BuOH reveals that the loss of ordering (i.e. conversion of hexagonal into wormhole) at 343 and 358 K (water-based) is not due to hydrolysis but to capillarity. This finding is remarkable since it is often thought that the loss of ordering is attributed to hydrolysis exclusively. This mesostructure suffers from extensive hydrolysis at 373 K, which explains the ordering loss even when dried in *n*-BuOH.

In terms of material dissolution, it was generally found that this is higher with increasing treatment temperature, but there is apparently no correlation with the hydrothermal stability. In fact the less stable material (Tc) dissolves less.

The two proposed solvent-routes are illustrated for the Tc material (Figs. 9 and 10), since Tc showed the most remarkable differences. In both cases hydrolysis takes place. Fig. 9 describes the pathways at 343–358 K. Route A includes hydrolysis and then a pronounced capillary stress during drying in water that finally gives

rise to a disordered shrunk structure. Route B, under low-surface tension, reduces the capillarity effect and the material can be better preserved in terms of ordering and texture. Fig. 10 describes the proposed two routes for the Tc material treated at 373 K; hydrolysis is so extensive that *n*-BuOH drying can only reduce shrinkage (Fig. 10b), which is extensively visible in the water-based route (Fig. 10a).

From this study, it can be learnt that for the Mc mesostructure, hydrolysis leads to loss of ordering, only at 373 K. For TAc, it was shown that capillarity leads to shrinkage in water. The Tc mesostructure reveals that capillarity is responsible for the loss of ordering and shrinkage at 343–358 K, while hydrolysis is responsible for the ordering loss at 373 K.

From the mechanistic standpoint, the proposed exchange solvent, *n*-BuOH, shows evidences that capillary effects play a role, however, its surface tension is still moderate. This means that the exchange/drying effectiveness may be enhanced by reducing the surface tension of the medium further. Another aspect that can play

Fig. 10. Suggested solvent-based pathways upon hydrothermal treatment at 373 K for Tc.

a role is the possible entrapped water, which has not been efficiently extracted with *n*-BuOH.

5. Conclusions

Interpretation of hydrothermal stability results for various types of MCM-41 materials has been done considering hydrolysis and capillary stress-induced effects, representing chemical and physical resistances, respectively. The latter effect is significant when the structure is not mechanically robust. Capillarity can give rise to two effects: shrinkage but also to loss of ordering during drying in water.

The Na-metasilicate based mesostructure is mechanically very stable and the hexagonal ordering remains up to 358 K but is lost at 373 K due to extensive hydrolysis. Such a high hydrothermal stability can be related to the exchanged CTA⁺ by Na⁺ or the high-applied ageing temperature, or both effects. The un-aged TEOS based mesostructure has the lowest hydrothermal stability, in terms of hydrolysis and rigidity, associated to the lack of an ageing step in the synthesis protocol. In *n*-BuOH, well-preserved hexagonal structures are obtained at temperatures of 343–358 K, while in water capillarity produces disordered wormhole and shrunk structures. At 373 K hydrolysis is extensive leading to a wormhole structure. The hydrothermally aged TEOS-based material shows a combined behaviour regarding the hydrothermal stability: the ordering is always maintained but the structure shrinks in water. Remarkably, this mesostructure has an excellent hydrothermal stability at high temperature, when compared to the other materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.micromeso.2015.08.024>.

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