Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name RSCPublishing

ARTICLE

Minute-made and low carbon fingerprint microwave synthesis of high quality templated mesoporous silica

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Hexagonal mesotructured templated silicas were produced in less than 10 minutes using an ultra-fast microwave assisted hydrothermal synthesis. Typically, 10 g can be prepared at once in a commercial microwave device usually devoted to analytical digestion. Undesired alcohol side-products were avoided using inexpensive water colloidal silica instead of silicon alkoxides as silicon source. In comparison with classical heating activation, the absence of pore expansion and pore wall thickening even for synthesis temperatures as high as 190°C, evidenced that heat transfer and diffusion of matter had no time to take place. Comparison between chemically extracted and calcined samples shows that the structure was better stabilized for autoclaving above 150°C. However, a fast temperature ramping and final temperatures above 180 °C were required to sear structures of the highest quality comparable to that of the best conventional methods. This is rationalized by assuming a sequential flake-by-flake assembly of the pore-wall at the micelle palisade. Notably, tosylate counterions yielded better structural characteristics than bromide counterions and allowed better opportunities for surfactant recycling.

We dedicate this article to our dear colleague Professor Pascal Perriat, who passed away before his time. He was a kind and joyful person, who offered us a lot of his time and knowledge.

Introduction

Among porous inorganic materials, one of the most cited and the most versatile is the surfactant templated mesostructured porous silica of MCM-41 type structure possessing a hexagonal array of 1D tubular nano-channels.[1-3] Discovered in 1992, this mesostructured porous solid, together with the cubic analogue MCM-48 and the lamellar MCM-50 analogue have revolutionized the field of porous materials in the mesopore range of sizes 2.5 to 7 nm.[1, 2] The advantage of this support is the very high surface area combined with tuneable porosity either by changing the length of the single carbon chain of the alkyltrimethylammonium surfactant or by adding some swelling agents.[1, 4, 5] This group of solids has been followed by other mesostructured materials prepared with other ionic surfactants, positively or negatively charged, such as alkylphosphonium, sulfonates and also neutral ones including diblock or triblock co-polymers.[6-10] They have been applied in many different fields such as catalysis, chromatography or storage owing to the unprecedented fine control of porosity in the nano range of sizes. Previously such control was known only for microporous solids such as zeolites.[11-13] Indeed, these solids open wide opportunities for molecular sieving and catalysis for large molecules and also allow internal functionalization with tuneable surface chemistry using organic silanes as grafting agents or directly in their synthesis leading to periodic mesoporous organosilicas (PMOS).[14-16]

The synthesis of all these materials is triggered by the nascent poly-anionic silicate oligomers growing at the micelle-solution interface below the critical micellar concentration of the templating surfactant. The growth follows a self-assembly mechanism.[17] The inorganic source is usually chosen from alkoxide type of molecules and also from other types of molecular precursors, allowing a wide variety of compositions typical of sol-gel chemistry.[18] To stabilize the structure and push forward the rate of condensation the solid is usually heated in an autoclave for several days. In the case of silica used in the original synthesis, the temperature is typically 100 °C for 1 day.[19] Shorter autoclaving times (~ 20 hours) can be afforded using slightly higher temperatures (130°C) and more hydrophobic counterions of the surfactant (tosylate, Tos^- instead of Cl^- or Br^-) as in the case of LUS mesoporous silicas.[20, 21] This timescale remains large in comparison to the rate of reaction for synthesis at the molecular level. In fact, film deposition of surfactant-templated materials on a flat surface develops within few seconds, according to a kinetics study using the so-called evaporation induced self-assembly (EISA) technique.[22, 23] Though hydrolysis and condensation of the alkoxide precursors is accelerated by fast evaporation of the alcohol, these syntheses are much faster than the classical syntheses with autoclaves and thermal heating.[24] In fact, by going beyond the convection limitation of classical heating, microwave synthesis of inorganic porous systems as short as 30 min to 1 h have been reported and concern mostly nanoparticles or zeolites.[25-29] As far as surfactant-templated silicas are concerned, there are very few thorough investigations of microwave-assisted synthesis, except triblock co-polymer templated SBA-15 or SBA-16.[30-32] To our knowledge, there are only two reports on well-structured cationic surfactant templated MCM-41 silica. The first one provides only anecdotal evidence and concerns a chromium modified version.[17] The second one is limited to structural optimization and eludes the question of stability, a crucial point treated here that requires temperatures much higher than those reported in that work.[33] Lately, Tang and co-workers reported an ultra-fast synthesis of MCM-41 (<5 min) in solution that was achieved using ultrasonic activation at room temperature.[34] Though large structure shrinking (> 10%) upon calcination was observed, the study reveals a somewhat poor stability. Therefore, easy, cheap, fast, reproducible and large-scale synthesis of thermally stable mesostructured materials remains to be demonstrated.

This paper tackles this problem using microwave heating that allows fast and homogeneous thermal activation, relatively large laboratory scale synthesis (up to 10 g at once) and potential industrial up-scaling. We focus on optimizing temperature ramping, plateau and duration under microwave irradiation using a commercially available analytical microwave oven for mineral digestion. The structure and the porosity of the materials were studied using X-ray diffraction (XRD) powder patterns and nitrogen sorption isotherms. The robustness of the silica framework was investigated comparing the structure and porosity after chemical extraction of the template (without calcination) and after calcination at 550°C. Investigation of the silica condensation was also performed using ^{29}Si solid state NMR, while the templating surfactant stability was estimated from ^{13}C solid state NMR. Surfactant recyclability was also treated using a simple acidic extraction.

Experimental

A) General procedures and methods

All the solids were prepared using cetyltrimethylammonium tosylate or bromide (CTATos and CTABr), both commercially available. The mother liquor had similar composition to that employed for classical hydrothermal treatments with some simplifications of the preparation for the sake of time saving, efficiency and further practical applications. Both MCM-41 and LUS silicas, templated by CTABr and CTATos, respectively, were synthesised using classical or microwave ovens.

B) Chemicals

CTATos and CTABr were provided by Sigma Aldrich and Alfa Aesar, respectively. Ludox HS-40 was purchased from Sigma-Aldrich and used to prepare both sodium and tetramethylammonium silicate solutions. TMAOH and Cab-O-Sil M-5 silica were purchased from Sigma Aldrich. Technical EtOH (96%) and distilled water were used for washing.

C) Synthesis of the reference MCM-41 (MBC)

MCM-41 silicas were prepared according to Reddy and Song's protocol[19] and classically prepared at 100 °C for 24 h. The authors optimized the silica source to obtain a highly structured material using sodium silicate, tetramethylammonium silicate and Cab-O-Sil silica. In our case, sodium and tetramethylammonium silicate stock solutions were synthesized as follows.

Synthesis of sodium silicate. Ludox (67.5 g, 1.13 mol) was added to sodium hydroxide (14 g, 0.35 mol) in 18.5 mL of water and stirred at 40 °C for 24 h.

Synthesis of tetramethylammonium silicate. Ludox (25 g, 0.42 mol) was added to tetramethylammonium hydroxide 20 wt% in water (38 g, 0.1 mol) in 37 mL of water and stirred at 40 °C for 24 h.

D) Synthesis of classical LUS silica (MTC)

Ludox (15.5 g, 0.26 mol) was added to sodium hydroxide (2 g, 50 mmol) in 50 mL of distilled water, then stirred at 40 °C until clear (*ca.* 24 h). A second solution of cetyltrimethylammonium *p*-toluenesulfonate (CTATos, Tos = *p*-toluenesulfonate, tosylate) (1.96 g, 4.3 mmol) in distilled water (71 mL) was stirred at 60°C during 1 h. In the meantime, the first solution (49 mL) was also stirred at 60°C during 1 h. Then the second solution was slowly added to the first one affording a gel molar composition: $1SiO_2/0.05CTATos/0.5NaOH/79H_2O$. The resulting mixture was further stirred at 60 °C for 1 h and transferred in a 200 mL autoclave to be heated in a classical oven at the desired temperature (130, 150 or 170 °C) for 20 h. Then the autoclave was allowed to cool first at room temperature for about 1 h and then in a water bath for about 10 min. The solid was then filtered on Büchner, washed with 100 mL of water and dried overnight at 80 °C to obtain an average of 3.8 g of white powder. Elemental analysis (wt%): MTC-130: Si: 23.61, C: 30.88, H: 6.56, N: 1.80, S. 0.39.

E) Synthesis of microwave MCM-41 (MBM)

A Berghof Speedwave oven was used for the synthesis of the mesoporous silica. It provides a microwave irradiation at 2450 MHz with a power of 1450 W. The protocol is similar to the classical protocol described above except that the solution was transferred in Teflon® autoclaves and heated at 150 or 180 °C, with a ramp of 1 min and a plateau of 9 min. Just after heating the Teflon® autoclave head is still cool so that each autoclave can be transferred manually into a cooling water bath (~12 °C) for half an hour. Then, the solution is filtered and the solid washed with distilled water before drying overnight at 80°C. Any protocol changes are stated in the text.

F) Synthesis of microwave LUS silica (MTM)

Before studying the influence of temperature, total protocol time was optimized for a synthesis temperature of 130 °C. The settings of the temperature profiles are detailed in Table S1.

Synthesis of microwave MTM-130-1 silica. The protocol is similar to the synthesis of MTC-130 except that the solution was transferred in two 100 mL pressured vessels (DAP-100) and heated in the microwave oven at 130 °C with a temperature ramp of 20 min and a plateau of 40 min. The autoclave was then cooled in air, and the solid was recovered according to the protocol described for the classical LUS silica.

Synthesis of microwave MTM-130-2, MTM-130-3 and MTM-130-4 silicas. The protocol is similar as previously, except that the first solution was added to the second one by pouring it on the edge of the recipient containing the surfactant. After a 2 min vigorous hand shaking, the mixture was transferred in the autoclaves and heated with different temperature profiles. MTM-130-2: 10 min plateau at 60 °C, followed by 10 min ramp and final 40 min plateau at 130 °C. MTM-130-3: 10 min plateau at 60 °C, followed by 10 min ramp and final 20 min plateau at 130 °C. MTM-130-4: 1 min ramp at 130 °C and 14 min plateau at 130 °C. The solid was recovered by following the protocol described above.

Synthesis of microwave MTM-130-5 silica. The protocol is similar to that for MTM-130-2, except that the mixture was heated at 130 °C with a ramp of 1 min followed by a 9 min plateau before cooling in a cold-water bath for 30 min. The solid was recovered according to the protocol described above. Elemental analysis (wt%): MTM-130-5: Si: 23.63, C: 30.91, H: 6.31, N: 1.72, S. 0.20.

The influence of temperature was studied by using this latter protocol. For the sake of clarity, the materials will be called MTM-*x* were *x* is the temperature of synthesis. Therefore MTM-130-5 will be named as MTM-130 in the following. Elemental analysis (wt%): MTM-150, Si. 23.71, C: 31.08, H: 6.41, N: 1.71, S: <0.20; MTM-170, Si: 24.17, C: 29.83, H: 6.17, N: 1.64, S: <0.20.

G) Extraction and calcination protocols

The surfactant was extracted by stirring 1 g of silica and 2 mL of HCl 1M in 200 mL of technical ethanol during 1 h. The solid was then filtered on Büchner, washed twice with 50 mL of technical ethanol and dried overnight at 80 °C to obtain the extracted material suitable for N_2 sorption isotherm and X-ray powder diffraction. The extracted solids were then calcined at 550 °C under an air flow for 5 h. Note that calcinations were performed after chemical extraction to minimize the quantity of organic burning and CO_2 production.

H) Characterization techniques

Nitrogen sorption isotherms at 77 K were determined with a volumetric device Belsorp Max on solids that were dried at 130 ºC under vacuum overnight. High and Low angle X-ray powder diffraction (XRD) experiments were carried out using a Bruker D8 Advance diffractometer with ultra fast detector VÅNTEC 1 using Cu-Kα monochromatic radiation. Elemental analyses were carried out by the Institut des Sciences Analytiques in Villeurbanne (France). Solid NMR spectra were measured on an Advance III Bruker 500MHz Wide Bore spectrometer, with a CP/MAS DVT (double resonance, variable temperature) probe 4 mm. The delay time between pulses (pulse width 5 µs) in HPDEC experiments was set to 500 s. Spinning speed was ~ 5 kHz and the number of scans was 5000 (frequency ^{29}Si = 99.36 MHz).

Results and discussion

A series of 2D hexagonal mesoporous silica was synthesized using microwave activation and cetyltrimetylammonium tosylate (CTATos) as a template to generate the porous mesostructure. These materials are denoted as MTM (T = tosylate, M = microwave) and are the object of this study. Two additional types of materials were also synthesized by classical (oven) heating and were used as comparisons: 1) 2D hexagonal mesoporous silica using CTATos as template (MTC, T = tosylate, C = classical heating), and 2) the classical MCM-41 silica using CTABr as template (MBC; B = bromide, C = classical heating). Finally, the corresponding MBM material with CTABr as template by microwave heating was also prepared. The materials synthesized under either thermal (which we use here interchangeably with “classical oven“) or microwave activation all adopted a 2D hexagonal array of channels that is typical of MCM-41 materials in the three different forms: the as-made form, then after chemical extraction of the template (-E), and finally after calcination (-C). All the XRD patterns presented a strong peak at 2° of 2θ scale, attributed to the basal 100 diffraction plan, and they presented at least two smaller peaks attributed to 110 and 200 reflexions (Figures 1 and S1, electronic supporting information).

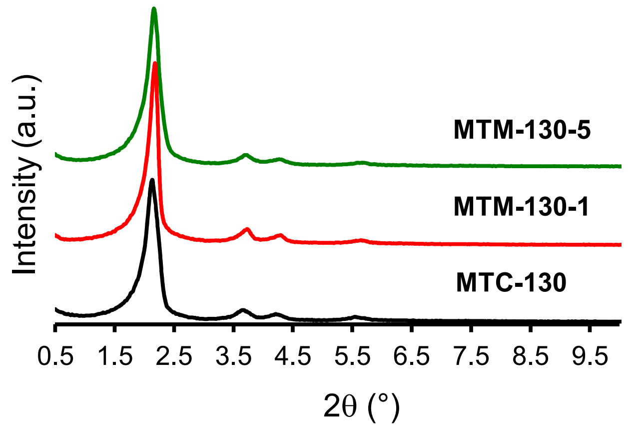

Figure 1 XRD powder patterns of as-made CTATos templated 2D hexagonal mesoporous silica prepared at 130 °C using classical heating (MTC-130) and microwave heating with different temperature profiles (MTM-130-1 and MTM-130-5, see experimental part).

A) Screening on as made materials

We synthesized the first series of as-made MTM materials at various microwave exposure times (from 3 to 60 min) and at various temperature ramps ranging from 1 to 20 min and at plateau temperatures of 130 to 190°C. In all cases, in respect of XRD they showed no noticeable changes, whether in peak position, line width or intensity (Figures 1 and S1). This structural similarity was mirrored by the absence of significant changes of the TGA profiles in this first series. In addition, Transmission electron microscopy (TEM) pictures of microwave-synthesized silicas were typical of regular MCM-41 materials (Figure S2). This series showed that microwave synthesis produced as-made materials with high quality structures within a period as quick as 10 minutes at 130 °C, and this for a temperature ramp as short as 1 min. In addition, the ramp rate, the temperature of the plateau and the duration of the plateau appeared to have little impact on XRD patterns. When compared with SBA-15 type materials, our results were widely divergent. These materials apparently show a very great enlargement of the pores under both conventional and microwave heating.[30, 32, 35] The SBA-15 series of Sanchez and co-workers confirms that the combined process of the self-assembly of the micelle and then the growth of the silica is very fast under microwave or ultrasounds, and also under evaporation induced self-assembly (EISA) conditions.[22, 23] The striking scarcity of literature on well-structured MCM-41 generated under microwave irradiation might appear surprising. This is so only if one omits the problem of the fragility upon surfactant removal treatments under chemical extraction or calcination.

B) Challenge, strategy and protocol of synthesis

Of all the stages in the above experiment, it is the condensation of silica occurring through the formation of Si-O-Si siloxane bridges that is, for us, the most important of the steps to control in order to achieve a fast synthesis. We must bear in mind that this process of condensation is a highly activated kinetic process, and one that is triggered much more by temperature than by reaction time. Accordingly, the highest temperature would be best, except that there is a potential degradation of the templating surfactant molecules, which takes place at *ca.* 130-150°C as shown for conventional thermal autoclaving.[36]

The highest temperature investigated here (190 °C) was reached with the shortest temperature ramp possible, which was 1 min with our current device. Higher temperatures (not investigated here) would have generated higher autogeneous pressure and an ageing of the Teflon lining of the autoclaves. In addition, to minimize the thermal inertia effect during the cooling time, it was decided to have an irradiation time of 10 min, and that figure includes the initial stages of heating (Figure 2). The temperature ramping was set from 1 to 10 minutes for the same total irradiation time. A reasonably efficient cooling was obtained by simple immersion of the autoclave in cool water for 30 minutes. Ice is not recommended to avoid thermal shock on the Teflon autoclave.

Furthermore, to better demonstrate the specificity of microwave activation and avoid any confusion with sol-gel composition, time, and other synthesis parameters, we had to set a consistent series of samples prepared using conventional thermal heating at various temperatures (Table 1). In all cases, the gel composition was kept constant, using either the classical procedure where the ammonium counterion is bromide for MCM-41, or tosylate for LUS.[20, 21]

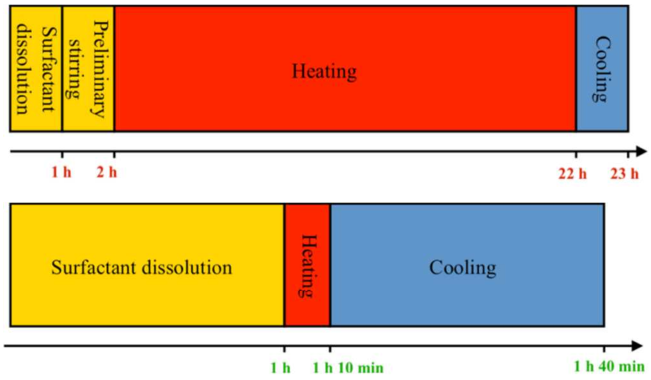

Figure 2 Gantt diagrams of the experimental protocol applied to classical (top) or microwave (bottom) thermal routes for hexagonal mesostructured porous silicas including the solution work out (ochre), heating (red) and cooling time (blue) steps.

The structural resistance to chemical, mechanical or thermal stress is directly related to the structure of the silica network. Indeed defects can be generated due to incomplete condensation of the silica network. It is an important parameter because the material is often calcined not only to remove the surfactant but also to consolidate the siliceous matrix by increasing the percentage of silanol condensation. Usually, solid state ^{29}Si NMR is a convenient technique to evaluate these imperfections based on the ratio of the Q^2 and Q^3 signals attributed to silanol groups, over the Q^4 signal of the bulk silicon atoms. However, the number of silanol groups involved in defects is rather marginal in comparison to that of the silanol located on the pore wall surface. Hence, more direct criteria were used instead. These included the structural changes undergone after calcination. Since the XRD cell parameters did not change much here, most of the reasoning adopted in the following paragraphs relied on the evolution of the specific surface area and pore volume (internal and external) either after chemical extraction of template or after calcination. A small variation of both pore volume and surface area would attest to pore wall densification and structure stabilization.

C) Evolution of porosity *versus* temperature using conventional heating activation

A series of mesoporous silicas were prepared (in agreement with the literature) at temperatures ranging from 100 to 170°C and using conventional heating using either bromine (MBC series for MCM-41) or tosylate (MTC series for LUS) as surfactant counterion.[36] Higher synthesis temperatures were avoided because of the decomposition of template that produces volatile side products (amines) and too high a pressure in the autoclave.[37]

The new data in the MTC series concerns the extracted MTC-E samples. It appeared that the structural parameter a_0 of the MTC-E-130/150/170 hexagonal mesophase underwent a slight increase from 4.8 to 5.0 nm up to 150 °C to reach a considerable expansion at 170°C (6.3 nm, entries 2 to 4, Table 1). This is mainly due to the pore expansion increasing from 4.0 to 5.3 nm while the pore wall thickening remains rather moderate (0.8 up to 1.0 nm). This is attributed to the thermal expansion of the micelles that apparently starts to take place here at 150°C and drastically increases at 170°C (Figure S3).[38] Concomitantly, the C_{BET} parameter of the BET equation exhibited a considerable increase from about 105 up to 211. These two increases are assigned to a profound surface restructuration, whereas there was no significant change of silanol concentration according to ^{29}Si NMR analyses. Note that the C parameter increases from a value close to that of calcined classical MCM-41 or LUS (C ~ 90, Table 1, entries 14 and 15) to get closer to that of a typical silica xerogel (C_{BET} = 230). This is in full agreement with our previous observations and it is assigned to a loss of surface roughness and reorientation of surface silanol groups leading to a higher surface polarity.[37] A better overview of all trends is provided in Figure 3. First, it appears clearly that the structural shrinkage decreases at higher autoclaving temperatures; the values for the shrinkage are Δa_0 = 0.3, 0.2 and 0.1 nm for 130, 150 and 170 °C, respectively. This somewhat small effect brings a first indication of a strong consolidation of the structure already at 130°C that is only slightly improved at higher temperatures. The internal pore volume V''_{int} evidenced a more considerable improvement with a loss upon calcination of -27, -6, -1 ± 2 % for 130, 150 and 170 °C, respectively. So we can see that the highest volume is obtained for the highest autoclaving temperature. The surface area is also a sensitive parameter, with a high value (above 1000 m^2/g) at l30°C, which also decreases significantly upon calcination (*ca.* 9%). In contrast, after autoclaving at 150°C, the surface area which remains quite large is unchanged after calcination, which indicates a stable pore size and a particularly stable structure. For autoclaving at 170°C, the smaller specific surface of about 850 ± 40 m^2/g is explained by much larger pores and the thicker pore wall. The full retention of the pore volume is also an indication of the full retention of the structure. In fact, these data compare well with an MCM-41 prepared at 150, 165 and 180°C for 48h with conventional heating with a_0 = 3.6, 4.1 and 4.4 nm for S_{tot} = 1190, 876 and 445 m^2/g and V_p = 1.28, 0.92 and 0.54 cm^3/g.[39]

Table 1 Porosity data from N_2 sorption isotherms at 77 K for 2D hexagonal mesotructured silicas after chemical extraction (-E) or after calcination at 550°C (-C)

Entry #	Material[a]	a_0[b] nm ± 0.1	S_{BET}[c] m^2g^{-1} ± 30	V'_{total}[d] cm^3g^{-1} ± 0.02	V''_{int}[e] cm^3g^{-1} ± 0.02	d_{BdB}[f] nm ± 0.1	$T_{w\ BdB}$[g] nm ± 0.1	C[h] ± 5
1	MBC-E-100	4.8	1140	2.08	0.98	4.0	0.8	110
2	MTC-E-130	4.8	1010	1.00	0.88	4.0	0.8	105
3	MTC-E-150	5.0	990	0.98	0.90	4.1	0.9	114
4	MTC-E-170	6.3	830	1.02	0.91	5.3	1.0	211
5	MTM-E-130	4.7	1020	0.98	0.87	3.9	0.9	86
6	MTM-E-150	4.6	910	0.90	0.75	3.8	0.8	88
7	MBM-E-150	4.9	990	1.88	0.87	4.1	0.7	114
8	MTM-E-170	4.5	900	0.89	0.76	3.8	0.7	87
9	MTM-E-180	4.6	990	1.00	0.86	3.9	0.7	135
10	MBM-E-180	4.9	1110	1.69	1.01	4.1	0.8	109
11	MTM-E-190	4.7	990	0.96	0.85	3.9	0.8	104
12	MTM-E-190-2’	4.9	1000	1.01	0.84	3.9	1.0	122
13	MTM-E-190-10’	4.8	1140	1.14	0.97	4.0	0.8	110
14	MBC-C-100	4.6	1070	1.86	0.81	3.7	0.9	87
15	MTC-C-130	4.5	920	0.86	0.73	3.7	0.8	87
16	MTC-C-150	4.8	1000	0.95	0.85	3.9	0.9	94
17	MTC-C-170	6.2	860	0.99	0.92	5.2	1.0	165
18	MTM-C-130	4.4	720	0.64	0.56	3.5	0.9	79
19	MTM-C-150	4.5	930	0.82	0.70	3.6	0.9	71
20	MBM-C-150	4.6	850	1.67	0.65	3.8	0.8	89
21	MTM-C-170	4.4	960	0.86	0.72	3.6	0.8	67
22	MTM-C-180	4.6	1000	0.93	0.79	3.7	0.9	79
23	MBM-C-180	4.6	880	1.50	0.79	3.7	0.8	87
24	MTM-C-190	4.6	1000	0.93	0.80	3.7	1.0	82
25	MTM-C-190-2’	4.6	980	0.92	0.76	3.7	0.9	93
26	MTM-C-190-10’	4.6	1030	0.97	0.82	3.7	0.9	92

a) see nomenclature in the text, note that 2’ and 10’ in entry 12 and 13 stands for the duration in minutes of the temperature ramp with no plateau, respectively b) $a_0 = d_{100}\times2/1.732$, hexagonal lattice parameter calculated from XRD, c) S_{BET} determined from BET equation surface applied in the relative pressure range of $0.05 \leq p/p_0 \leq 0.16$, c) V'_{total} at $p/p_0 = 0.99$ including inter grain void volume d) V''_{int} extrapolated at $p/p_0 = 0$ on the adsorption plateau of the t-plot, including only the mesoporous internal volume , e) $Y = 14{,}60994 + 74{,}67812X - 81{,}96198X^2 + 155{,}8457X^3$, $X = P/P_0$ ($0.11 \leq P/P_0 \leq 0.50$), Y = pore diameter (in Å), accuracy ± 0.1, f) T_w, pore wall thickness and h) BET C parameter correlated to the sticking coefficient of N_2 with the surface.

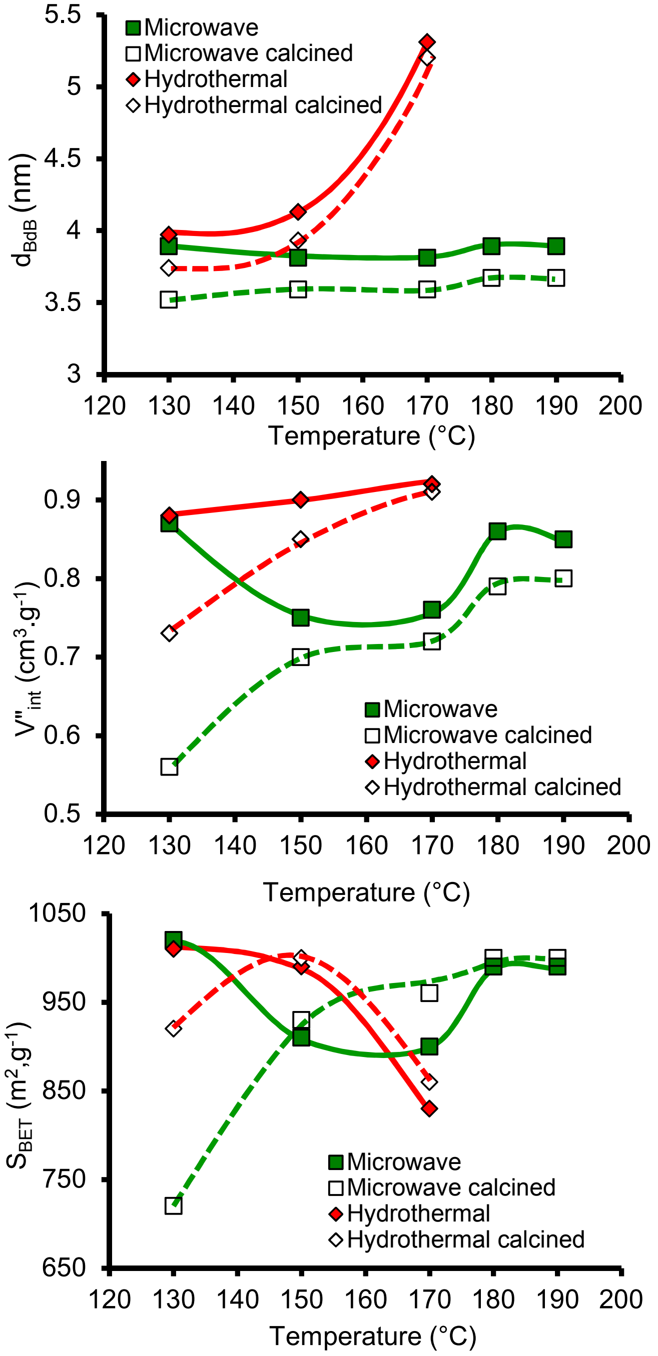

Figure 3 Temperature effect on pore diameter, d_{BdB} (top), pore volume, V''$_{int}$ (middle) and surface area S_{BET} (bottom) of materials prepared according to classical (red lines) or microwave thermal activation (green lines) for chemically extracted (full lines) or calcined (broken lines) samples. The lines provide a guide to underline the evolution without any mathematical fitting nor theoretical meaning.

The MCM-41 (Br^- counterion) usually prepared at 100°C presents similar characteristics than the LUS prepared at 130°C (Table 1, entries 1 and 2). The main difference consisted of a very large external volume of about 1.10 cm^3, which was reminiscent of intergrain voids formed by aggregation of small MCM-41 particles. The external volume remained nearly constant upon calcination (Entry 14). As far as loss of internal pore volume upon calcination is concerned, the stability of MBC-100 (-18% loss) lies in between that of LUS prepared at 130°C (-27 % loss, MTC-130) and LUS prepared at 150°C (-6 % loss, MTC-150). These observations outline clearly that the best autoclaving temperature that yields high quality stabilized LUS in 20 hours is 150°C. However, to produce a higher stable solid with thicker pore wall and larger pores, one would need temperatures above 170°C or even more.[37, 39]

D) Evolution of porosity *versus* temperature for microwave heating activations

For the microwave series MBM of MCM-41 using Br^- as surfactant counterions, only two temperatures were tested (entries 7 and 10 for extracted samples, and 20 and 23 for the calcined ones). This series will be described after the more complete microwave series MTM of LUS (Table 1: entries 5, 6, 8, 9 and 11 for chemically extracted and, 18, 19, 21, 22 and 24 for calcined materials). The only parameter changed was the temperature, while the ramping rate was the fastest, namely between 1 and 2 min (due to the power limitation of the machine) for a total duration of 10 min.

The MTM series confirmed the absence of thermal expansion of the structure from 130 up to 190°C (a_0 = 4.5-4.7 and 4.4-4.6 ± 0.1 nm, before and after calcination, respectively). This is the first important difference with the classical thermal activation. Focusing first on the chemically extracted non-calcined materials, *i.e.*, on the MTM-E series (Table 1: entries 5, 6, 8, 9), it appeared that both pore diameter (3.9 ± 0.1 nm) and surface area (960 ± 60 m^2/g) are rather similar to that of the low temperature conventional MTC-E series (Figure 3). Indeed, the pore wall was relatively insensitive to the temperature and similar to that of the conventional low temperature MTC-E series (0.8 ± 0.1 nm). The highest deviation was found for slow temperature ramping (see discussed below, Table 1, entry 13). The most surprising difference concerns the internal volume that reached a minimum for intermediate temperatures of 150 and 170°C (V''$_{int}$ of *ca.* 0.75 instead of *ca.* 0.86 cm^3/g). This effect was readily observed on the N_2 nitrogen sorption isotherms exhibiting a lower plateau of adsorption (Figure 4). This is assigned to a partial collapse of the structure evidenced by a higher uptake at $p/p_0 > 0.9$ due to the formation of much larger pores (∅ > 100 nm).

As far as the structural shrinkage under calcination is concerned, the microwave MTM series was also relatively insensitive to the temperature plateau (a_0, Table 1). Concomitantly, the pore diameter decreased very lightly (shrinkage of *ca.* -11% at 130°C and 5 % or less above) and compares well with the most stabilized conventional MTC-150 material. Again, this is the internal pore volume that is the most affected by calcination. MTM-130 is less stable (internal pore volume loss of -36 %) than the classical analogue MTC-130 (-27%). Higher temperatures (≥ 150°C) were necessary to observe stabilization (-9 to -6 % internal pore volume loss). The surface area loss upon calcination was also maximal (-30%) for

130°C and minimal at 180°C or above (Figure 3). Surprisingly, at intermediate temperatures (150 or 170°C) there was no loss of surface area despite the loss of mesopore volume. By contrast, the MTM-E materials exhibited a minimum up to the point where the surface was smaller before than after calcination for MTM-170. While a surface loss is easy to understand upon the effect of a structure collapse, an increase is more surprizing unless one invokes a dismantling of the solid into small facetted flakes, thereby exposing more surface than the initial assembly into channels (Figure 5). This effect should increase for higher – but still moderate – dismantling where flakes cannot accumulate enough to merge one with another. This clearly evidences that full stabilization cannot be claimed for temperatures of 170°C, where this dismantling effect is important, and it overcomes the loss of surface due to the loss of the mesopores. Therefore, at such short time of autoclaving, temperatures of 180 °C or above are necessary to obtain a fully preserved honeycomb array of channels typical of hexagonal 2D mesoporous silica (LUS and MCM-41).

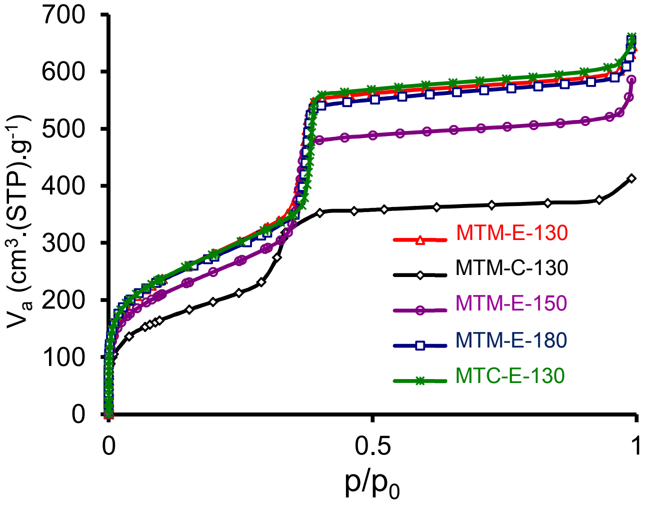

Figure 4 Comparison of N_2 adsorption isotherm profiles at 77 K of MTM-E-130 (red line), MTM-C-130 (black line), MTM-E-150 (violet line), MTM-E-180 (blue line) and MTC-E-130 (green line, taken as a reference).

The absence of pore expansion upon temperature from 130 to 190 °C is a striking feature. It suggests that the channel – if it is correctly formed – can easily resist the internal pressure that is provoked by the thermal expansion of the micelle. This effect was observed at least between 150 and 170 °C, under which circumstances a part of the structure is damaged. Obviously, this detrimental effect can be avoided if the temperature is not maintained constant for 150-170°C, in what could be called a 'temperature window of instability'. Prolonging the ramping profile from 1 to 10 min (with no plateau) should produce a less structured system. However, the corresponding material MTM-E-190-10' presents a higher surface area, higher internal pore volume and larger C_{BET} parameter for the chemically extracted materials. Nonetheless, it is much less stable upon calcination (ΔV_{pore} ~ -16% instead of 6%, ΔS_{BET} ~ -10%, instead of 1%,). Conversely, the suppression of the plateau revealed that a very rapid temperature increase to 190°C (namely, 2min) yielded a better material (ΔV_{pore} ~ -10% upon calcination), though not as good as when a temperature plateau is applied. All these observations suggest that ultra-fast synthesis can overcome the detrimental effect of micelle thermal expansion, which is probably the driving force for the partial dismantling and pore expansion under much longer classical thermal heating processes illustrated by the MTC series.

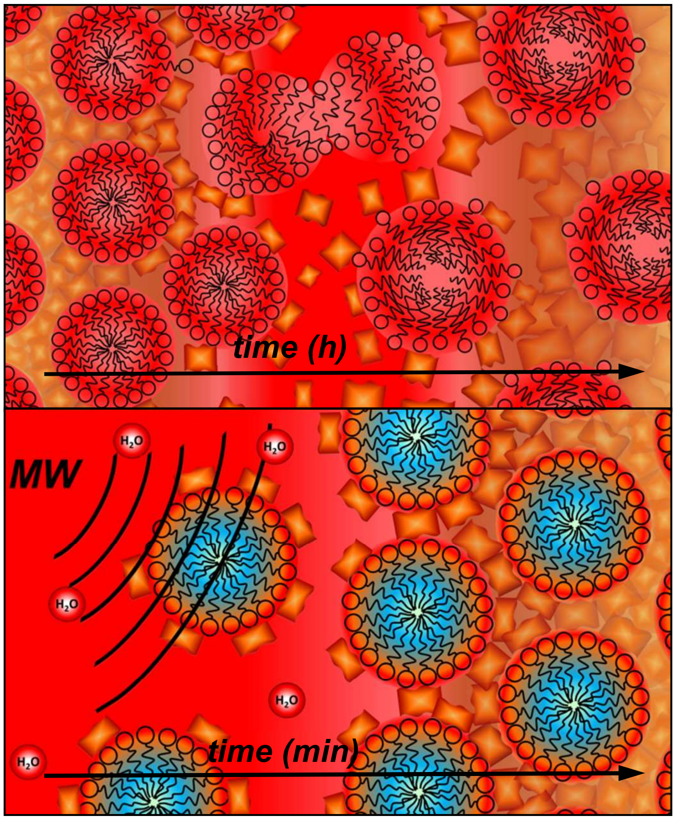

Figure 5 Condensation reactions of silanol moieties and silicate condensation around micelles with classical heat diffusion (top) or microwave activation (bottom).

E) Crystal growth, stability and microwave specificity

The ultrafast formation of surfactant templated silica was first shown using ultrasonic activation that is known to create locally high temperature and pressure.[34] The present results fully confirmed that such fast syntheses (2 min up to 190°C) can lead to a stabilized LUS or MCM-41 structure without the assistance of a substrate as it occurs during the formation of film using the EISA technique.[24] Such result is questioning the type of growth mechanism at stake and the relation with the structure and stability observed here. One may also question the specific role of microwave in comparison with other type of thermal activation process.

The morphology of the solid is less fibrous than the material prepared by conventional heating. Indeed, according to scanning electron microscopy, the higher the temperature the smaller the number of fibres and the higher the formation of spherical grains (Figure S4). Such an effect was also observed for high temperature synthesis using conventional heating and may not be related to the microwave effect.[36]

Obviously, the stability and the variation of the C_{BET} parameter in the present series prompted us to probe the nature of the defects and more particularly the fraction of silanol groups that may fingerprint the level of the silica condensation. Strikingly, no particular difference was found between the ^{29}Si solid-state NMR spectra of the classical and the microwave series as well as in each series (Figure S5, Table S2). As expected, there was a higher proportion of bulk $[Si\text{-}(OSi)_4]$ species when the MTM materials were prepared at higher temperature. It is likely that observations made on stability described above likely concern a too small fraction of silanol groups to be resolved using solid state NMR.

Nonetheless, the formation of small pore wall debris under calcination invokes the possibility of a block-by-block growth as observed for zeolites synthesised using similar sol-gel routes.[40-42] In this model, the growth rapidly yields crystallized rafts of 2 x 2 x 8 nm that progressively stick together into larger blocks of 10 to 20 nm themselves assembled into particles of about 80 to 120 nm large. The main difference here stems from the absence of both crystallization and well-organized surface. The block-by-block growth mechanism in the presence of surfactant template has been also proposed to explain the different morphologies that can be generated in templated mesoporous silica nanoparticles (MSP).[43] Here, the growing pieces of matter would better be called *flakes* rather than *blocks* for their rather amorphous nature. Their growth in symbiosis with the micellar tubes followed by their progressive merging will create a lot of imperfections. Such inorganic flakes imperfectly covering the organic tubules would resemble fontanels of an immature skull of an infant. Ill-covered micelles and their assembly into larger objects were also proposed by some of us to explain different morphologies observed for silica nanoparticles.[43] This model explained the above observation assuming that the connectivity between flakes (fontanels) remains weak enough below 130°C and can break back into flakes or debris that may produce higher surface area while they appeared consolidated above 150°C. With respect to NMR, this solidification by merging the flakes one to another occurs at the very last step of the wall condensation, implying a rather weak variation of the number of silanol groups in comparison to that of those exposed on the internal surface of the channel.

According to Ergun *et al.*, 90°C or 120 °C for longer time of equilibration under microwave up to 60 min, the pore diameters were 4.2 and 4.8 nm at 90°C and 120°C, respectively.[33, 44] Such a pore expansion is interpreted here as flake by flake seal-and-unseal process allowing to adaptation to a larger pore diameter. The rather small capillary condensation of these materials indicates that about half of the mesopores were destroyed at 550 °C for such low temperatures. Then, the rather elevated high surface area up to *ca.* 1400 m^2/g in that report is attributed according to our model to dismantled flakes that accumulate randomly in channels and not yet collapsed one with the other. Besides, the diameter measured by Ergun *et al.* at 90°C is similar to that of the actual MTM series synthesized up to 190°C. If one consider the pore diameter as an indicator of the temperature at which the proto-channels are formed and determine the pore diameter, this indicates that in the present study the irradiation time was short enough to avoid reconstruction to occur even between 90°C and 130°C, a temperature range at which the structure is not fully consolidated. Indeed, Ergun *et al.* observe a pore expansion at 120 °C for a temperature plateau of 30 minutes. This suggests that, the consolidation takes place by progressive merging of the flakes of the immature walls and explain that it has to be done fast to sear the structure before the detrimental effect of the micelle thermal expansion. Note also that the structural shrinkage that remains above 170°C up to 190°C (~ 6%) is similar to that of a conventional thermal autoclaving at 150°C for 20 hours as in MTC-150 material. This last structural retraction is obviously more difficult to achieve though it takes place without structural damage and is rather a mere silica densification of the wall. All the maturation levels proposed here occurs before any crystallization may take place according to the absence of any diffraction peak above 7° in 2θ up to 190°C (figure S6).

Therefore, the stability of the best material reported here should be equivalent to that of a classical MCM-41 prepared using a conventional heating and autoclaving at a temperature of *ca.* 150 °C (see above), which is better than most of the reported MCM-41 but less than super-stable mesoporous silicas. In fact, the latter are prepared in quite radical autoclaving conditions, *i. e.,* 180 or 190°C for several hours, respectively and present a large deterioration of their XRD patterns and adsorption capacities in contrast to the present materials.[39]

The mechanism proposed here is evidenced either thanks to the capacity of microwave radiation to increase the temperature rapidly all through the sample or favoured via a specific microwave activation of the silica polycondensation. Indeed, the latter occurs at the micelle palisade, which is the most polar region of the solution where microwave may generate local overheating. Specific microwave effects are often invoked to explain some reactions to the expense of others (selectivity). Nonetheless, it is not clear yet whether it affects the activation of specific polar functions, promotes inhomogeneous heating of the solution or modifies the transition state.[26-27] The scheme of figure 5 that represents blue coloured micelle interior with the rest of the solution in red colour may suggest an inhomogeneous heating effect or simply the absence of effective thermal expansion of the structure, the question remains open. To fully address the question very fast conventional heating synthesis would be required for comparison. Such investigation is in progress.

F) Characteristics of a high quality LUS or MCM-41

The literature is rich of several thousand papers reporting a rather large variety of characteristics for MCM-41 type of structure claiming success with surface as high as 1400 m^2/g, or pore volume as high as 1.5 or even 2 cm^3/g. All these characteristics might be interesting *per se* though they remain confusing if one as no reference to refer to and no explanation of any deviation from it. From the present study, one can draw a more precise range of characteristics defining ideally well-structured templated mesoporous silica using a single C-16 chain quaternary ammonium of alkyltrimethylammonium type from XRD and nitrogen sorption measurements:

i) **for the chemically extracted form**, a_0 = 4.7 - 4.9 nm, d_{BdB} = 3.5 - 4.1 nm, T_w = 0.8 – 1.1 nm, S_{BET} = 960 - 1020 m^2/g, V''_{int} = 0.75 – 0.91 cm^3/g and C_{BET} = 100 – 120.

ii) **for the calcined form (550 °C for 5 h)**, a_0 = 4.4 - 4.8 nm, d_{BdB} = 3.5 - 3.9 nm, T_w = 0.7 - 1.1 nm, S_{BET} = 950 - 1010 m^2/g, V''_{int} = 0.75 - 0.91 cm^3/g and C_{BET} = 100 – 120.

A non-stabilized structure with lot of defects in the pore wall would exhibit a surface area above the ideal values while the internal pore volume would remain in the expected range. If instead the volume is below the ideal range for super large surface area while higher microporosity appears to the expense of mesoporosity, on deals with a partially collapsed calcined structure. Large external volume is indicative of void between mesoporous nanoparticles.[43] Consistently, the inter-particle void should decrease under calcination due to particle merging Note that the MCM-41 prepared using Br^- as template counterion is an illustration of this situation. Larger pore size would indicate the formation of a reconstructed structure under long time exposure or high temperature autoclaving. Within this frame of observations, it appears that the best conditions of synthesis are 150°C for 20 h for conventional heating while it is 180 or 190 °C for a plateau of 10 minutes or 2 minutes, respectively as exemplified by materials MTC-150, MTM-180-10 or MTM-190-2’. Note that the tosylate is a better counterion than bromide.

G) Lowering the carbon fingerprint

Usually, the duration of the conventional heating treatment lasts for 3 to 7 days depending on the temperature of autoclaving (average of 7200 min). The microwave oven uses about the same electric power than the conventional oven for a duration that is about 1000 times shorter so the gain of energy is three orders of magnitude. To improve further the carbon fingerprint, evaluation of the proportion of surfactant recycling was demonstrated. An extraction using 1 eq *p*-toluenesulfonic acid extracted 70% of the surfactant that was recovered by evaporating the solvent under vacuum. According to TGA and solid-state ^{13}C NMR analyses, cetytrimethylammonium *p*-toluenesulfonate (CTATos) is recovered (purity > 95%) and lead to material none discernable from those obtained with the commercial surfactant according to XRD and porosity measurements. The remaining 25 % can be recovered easily by acidic treatment using acid methanol solution as already reported for the cubic MCM-48 mesoporous silica.[45] Such chemical extraction can be also conducted using ethanol (a less toxic and greener solvent) to replace methanol as proposed by some of us.[46, 47]

Conclusions

Reproducible ultra-fast gram scale syntheses of highly ordered 2D hexagonal mesostructured porous silicas were performed from an aqueous colloidal silica solution in the presence of trimethylcetylammonium (CTA^+) template using a microwave activated hydrothermal route. Though high ordering was achieved at relatively low temperature (< 130°C in the present study, and as low as 90°C according to literature), fast temperature ramps combined with final temperatures as high as 180-190°C were needed to sear a structure of high quality. The partial collapse at low temperature up to 170°C that may produce higher surface area is rationalized in terms of dismantlement of pore wall fragments reminiscent of a flake-by-flake growth mechanism of the pore-wall. At intermediate temperatures of 150 and 170°C, loss of pore volume was attributed to partial collapse reminiscent to imperfect merging between flakes. The absence of thermal pore swelling and negligible pore thickening up to 190°C revealed that both mass and heat transfers were avoided due to the very short synthesis time. A relatively small but still present shrinkage under calcination for synthesis performed above 170°C suggests that the last step of consolidation is the silica condensation inside the pore-wall. In addition, more hydrophobic template counterions such as tosylate favours the silica growth in comparison to bromide counterions that produce more external surface from inter grain voids. In any case, it is shown here that microwave activation is not only time and energy saving but also cleaner since it applies on cheap and recyclable aqueous colloidal silica precursor as well as on tosylate salts of CTA^+ that can be conveniently recovered and recycled.

Acknowledgements

The authors thank the KAUST funding grant. J. C. thanks the French “Ministère de l’Enseignement, de la Recherche et de la Technologie” (MERT) for a PhD fellowship, and the C-MIRA program of Rhône-Alpes region in France for financial support.

Notes and references

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Electronic Supplementary Information (ESI) available: [complementary characterization of the materials including 1 Table and 6 figures]. See DOI: 10.1039/b000000x/

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44. Note that the BdB method leads to pore size values close within 0.1 nm to those obtained from DFT and both techniques are more reliable methods than commonly used BJH, which provides values 0.7 nm smaller, i. e., 3.0-3.2 nm often reported for MCM-41 templated by cetyltrimethylbromide, CTAB. For smaller values the difference increases, for instance 2.2 nm (BJH) for 3.0 nm (BdB).
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Graphical abstract:

Minute-made and low carbon fingerprint microwave synthesis of high quality templated mesoporous silica

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Microwave heat activation allows to sear in few minutes high quality MCM-41 like mesoporous silicas with no structural expansion up to 190°C likely through a flake-by-flake assembly of the pore-wall at the micelle palisade.