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Protocol optimization for the mild detemplation of mesoporous silica nanoparticles resulting in enhanced texture and colloidal stability

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ABSTRACT

Porosity development of mesostructured colloidal silica nanoparticles is related to the removal of the organic templates and co-templates which is often carried out by calcination at high temperatures, 500–600 °C. In this study a mild detemplation method based on the oxidative Fenton chemistry has been investigated. The Fenton reaction involves the generation of OH[•] radicals following a redox Fe³⁺/Fe²⁺ cycle that is used as catalyst and H₂O₂ as oxidant source. Improved material properties are anticipated since the Fenton chemistry comprises milder conditions than calcination. However, the general application of this methodology is not straightforward due to limitations in the hydrothermal stability of the particular system under study. The objective of this work is three-fold: 1) reducing the residual Fe in the resulting solid as this can be detrimental for the application of the material, 2) shortening the reaction time by optimizing the reaction temperature to minimize possible particle agglomeration, and finally 3) investigating the structural and textural properties of the resulting material in comparison to the calcined counterparts. It appears that the Fenton detemplation can be optimized by shortening the reaction time significantly at low Fe concentration. The milder conditions of detemplation give rise to enhanced properties in terms of surface area, pore volume, structural preservation, low Fe residue and high degree of surface hydroxylation; the colloidal particles are stable during storage. A relative particle size increase, expressed as 0.11%·h⁻¹, has been determined.

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1. Introduction

Since the discovery of structured mesoporous materials [1] interest was raised in the synthesis of colloidal mesoporous silica nanoparticles (MSN) [2,3], mostly for medical applications. Careful control of the particle shape and size has been challenging targets, which has led to a remarkable effort in the field. The initial attempts were based on the modification of the Stöber method, using alkylammonium surfactants [4–10]; where spherical micrometre-sized particles are obtained. MSN with smaller sizes could only be synthesized when dilution was applied in order to lessen the crystal growth and favouring nucleation [11–16].

Additional developments in synthesis arrived after using particle growth inhibitors. For instance, the addition of co-templates, such as the block copolymer Pluronic F127, controls the secondary extra-particle porosity of hexagonally ordered MSN [17] and MCM-48 nanoparticles [10], forming well-defined secondary pores. Triethanolamine as chelating and mineralizing agent has been proposed, giving rise to stable suspensions of mesoporous silica with sizes ranging 50–100 nm [18–20]. The particle size could be further reduced to 20 nm when applying dilution to TEA in combination with tetramethoxysilane or bis(triethoxysilyl)-ethylene [21–25]. Organic amines in combination with surfactant counterions are claimed to tune the channel morphology [26]. In a different route, L-lysine and L-arginine create 3D arrangements of silica nanoparticles [27] while the functionalization with poly(ethylene)glycol silane (PEG-silane) keeps a good particle dispersity [28,29]. Particle growth can also be controlled by the addition of a

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PEG-silane, allowing the growth of ultra-small nanoparticles, from 6 nm to larger than 15 nm [30,31].

Coupled to the synthesis, an important aspect in the porosity development relates to the removal of the organic templates and co-templates. Conventionally, calcination has been applied, which consists of a thermal treatment in air at temperatures of 500–600 °C. Such a treatment completely removes the surfactant and condenses the structure further. Alternatively, mild methods to remove the template of MSN have been proposed in order to maximize the pore volume, avoid or minimize particle aggregation and to maximize the surface hydroxyl groups. Ethanolic extraction aided by HCl or NH_4NO_3 [32] is a relatively simple method that requires various extractions to fully eliminate the template. Surfactant removal by dialysis of the as-made colloidal suspension [21] removes completely the template and retains the original particle dispersion. High-boiling-point alkylphosphines have been proposed, showing no unit cell shrinkage, no particle aggregation and a more condensed network [33].

In this study a mild detemplation method, based on the oxidative Fenton chemistry has been investigated on a colloidal suspension of MSN. The Fenton reaction involves the generation of $\text{OH}^\bullet$ radicals following this redox cycle:

The hydroxyl radical then acts as oxidizing agent to oxidize the organic template according to reaction (3):

where CO_2 , H_2O are the final oxidation products. $\text{MSN}(\text{CTAC})$ corresponds to the template-containing mesoporous silica nanoparticles and $\text{MSN}(\)$ is the template-free counterpart.

De Laat and Le reported that reactions involving halogen radicals occur and are much faster than $\text{OH}^\bullet$ radicals [34]. As the CTAC template (cetyltrimethylammonium chloride) employed in this study contains Cl^- , this can also be oxidized to form dichloride anion radicals, $\text{Cl}_2^{\bullet-}$ (4)–(6):

It was demonstrated that in the presence of Cl^- , the dichloride anion radicals ($\text{Cl}_2^{\bullet-}$) are the dominating oxidizing species [34]. Therefore the following oxidative pathway is also considered (7):

Besides the main reactions, other competing reactions (8)–(13) occur as well, which implies that the selection of the reactions conditions is of crucial importance to avoid wasting H_2O_2 :

This work reports the optimization of the template removal procedure via the Fenton chemistry for a MSN, using different conditions to those previously reported [35,36], aiming at the reduction of Fe concentration to avoid side effects in the application field. A second goal was shortening the detemplation time in order to maintain the particle dispersion, since a prolonged reaction time under highly exothermal and hydrothermal conditions may lead to particle aggregation via condensation reactions. The derived optimal material was structurally and texturally characterized, and compared to the calcination counterparts.

2. Experimental methods

2.1. Materials

Cetyltrimethylammonium chloride (CTAC, 25 wt.% in H_2O), tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$, 98.0%) and triethanolamine (TEA, 98%) were acquired from Sigma–Aldrich. Hydrochloric acid (37 wt.%), absolute ethanol (EtOH, >99.9%), H_2O_2 (30 wt.%) were purchased from Merck.

2.2. Synthesis

The mesoporous colloidal silica-based material (MSN) was synthesized based on the route reported by Möller et al. [18]. In a typical experiment, a mixture of 2.3 g (15.7 mmol) of triethanolamine, 32 g (1.78 mol) Milli-Q water, 5.2 g (4.05 mmol), CTAC (25 wt.% in H_2O), 4.5 g (75 mmol) absolute ethanol was pre-heated at 60 °C for 20 min under stirring at 400 rpm speed. Then 3.65 mL (16.25 mmol) of TEOS were added dropwisely into the mixture within 2 min. The colour of the mixed solution turns to light blue in

Table 1
Summary of studied materials with their preparative conditions.

Entry	Material	Preparative conditions
1	MSN-D	Hydrolysed nanoparticles, directly dried by solvent evaporation at 80 °C for 12 h
2	MSN-C	Hydrolysed nanoparticles, centrifugation to remove mother liquid and unbound CTAC template, drying at 80 °C for 12 h
3	MSN-W1	Hydrolysed nanoparticles, centrifugation to remove mother liquid, H_2O addition/centrifugation and drying at 80 °C for 12 h
4	MSN-W2	Hydrolysed nanoparticles, centrifugation to remove mother liquid, H_2O addition/centrifugation (two times) and drying at 80 °C for 12 h
5	MSN-W3	Hydrolysed nanoparticles, centrifugation to remove mother liquid, H_2O addition/centrifugation (three times) and drying at 80 °C for 12 h
6	MSN-Fopt	Fenton chemistry-based detemplation applied to the MSN-D mesophase at optimal conditions, i.e. 90 °C for 3 h, and dried at 80 °C for 12 h
7	MSN-DC	Calcination of MSN-D mesophase, 550 °C, 6 h, 1 °C min ⁻¹
8	MSN-CC	Calcination of MSN-C mesophase, 550 °C, 6 h, 1 °C min ⁻¹
9	MSN-W1C	Calcination of MSN-W1 mesophase, 550 °C, 6 h, 1 °C min ⁻¹
10	MSN-W2C	Calcination of MSN-W2 mesophase, 550 °C, 6 h, 1 °C min ⁻¹
11	MSN-W3C	Calcination of MSN-W3 mesophase, 550 °C, 6 h, 1 °C min ⁻¹

Fig. 1. a) TGA in air of the mesophase decomposition, calcined and optimal Fenton (90 °C, 3 h; denoted as MSN-Fopt); b) DTGA patterns; c) temperature effect of the Fenton demetallation, reaction time was always 24 h; d) effect of reaction time at 90 °C, with and without Fe(III)–nitrate catalyst addition, denoted as Fe(II/III) as in practice both redox species co-exist.

10 min, which indicates the nanoparticles formation. The resulting mixture, having a molar composition of 1 TEOS:0.25 CTAC:0.97 TEA:4.62 EtOH:109.4 H₂O, was then stirred (400 rpm) at 60 °C for 2 h.

Depending on the post-treatment, the solid was handled differently as discussed below for each particular case. Before characterization, the MSN sample was dried at 80 °C for 12 h.

2.3. Fenton-chemistry based demetallation

In a typical Fenton demetallation reaction, a suspension is made by mixing 2 mL of the MSN suspension and 20 mL H₂O₂ (30 wt.% Merck) in a 100 mL round-bottom flask at room temperature. Then 20 µL Fe(NO₃)₃·9H₂O from a stock solution (2.5 g in 50 mL) was added. The as-obtained mixture was heated to the reaction temperature (30–90 °C), in a preheated oil-bath equipped with a

condenser, for a period ranging between 1 and 24 h. After the reaction took place, a fraction of the suspension was analyzed by dynamic light scattering (discussed in Section 2.5), and the remaining solution was centrifuged at 17,000 rpm for 30 min (Beckman coulter equipped with a rotor type JA-17). The resulting material was dried at 80 °C for 12 h.

2.4. Calcination

The particles suspension was separated by centrifugation at 17,000 rpm for 30 min (Beckman coulter, rotor type JA-17). The sample was then subjected to sonication in H₂O for 5 min followed by centrifugation. This process was carried out up to 3 times. The resulting materials were dried at 80 °C for 12 h. The samples were coded as NS-W1, NS-W2 and NS-W3, where the number indicates the number of washing steps.

Table 2

Properties of mesophase and final materials: CTAC template content, carbon and silanol concentrations, DLS-based particle size and Fe content.

Material	CTAC (wt.%) ^a	Carbon (wt.%) ^b	Si–OH (wt.%)	D _{DLS} (nm)	Fe ^{ICP} (ppm)
MSN-D	80.2	55.6	–	196	B.D.L. ^c
MSN-DC	0.9	0.2 (>99)	1.1	179	B.D.L. ^c
MSN-Fopt	4.4	0.5 (99)	7.1	194	85

^a Determined from the TGA weight loss between 150 and 900 °C.

^b Value between parenthesis corresponds to the demetallation efficiency compared to the starting MSN-D mesophase.

^c B.D.L. = below detection limit.

Fig. 2. SAXS patterns for various relevant MSN materials.

Two additional protocols were investigated. In one case, the synthesized colloidal suspension was directly dried (80 °C, 12 h) without any separation or washing step, leading to the MSN-D material. In another case, the sample was centrifuged in order to remove the unbound CTAC template and dried afterwards, resulting in the MSN-C material.

All these materials were calcined at 550 °C for 6 h at 1 °C min⁻¹ using a LT9/11 Nabertherm furnace. Suffix “C” in the samples’ code indicates that the material has been calcined.

Table 1 summarizes the preparative conditions of the investigated materials.

2.5. Characterization

Small angle X-ray scattering (SAXS) measurements were carried out at room temperature using 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 CuK α radiation beam with a full width at half-maximum of about 0.2 mm at the sample position. The sample-to-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⁻¹.

Thermogravimetric analysis (TGA) was carried out with a TGA/SDTA851e Mettler-Toledo apparatus using synthetic air (100 mL NTP min⁻¹) by heating the sample at 10 °C min⁻¹ from 30 to 900 °C. DTGA in the graphs refers to the derivative of the TGA pattern.

Nitrogen physisorption analyses were carried out in a Micromeritics ASAP 2420 apparatus at liquid nitrogen temperature (−196.2 °C). Prior to the analysis, the samples were degassed in vacuum at 350 °C for 10 h. The surface area (S_{BET}) was calculated using the standard BET method. 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 distributions (PSD) were obtained from the BJH method using the

Fig. 3. TEM images (300 kV) of relevant MSN materials: a) MSN-DC and b) MSN-Fopt.

Fig. 4. Hydrodynamic diameter distributions for various relevant MSN materials.

adsorption branch of the isotherm. The maximum of the PSD was taken as representative diameter, denoted as $\phi_{\text{BJH}}^{\text{in}}$, where the 'in' superscript indicates the intraparticle pore size.

CHN elemental analyses were carried out in a EuroVector 3000 CHNS analyzer. All analyses were done in duplicate to verify possible sample heterogeneity. For these materials the standard deviation was <2%. The protocol consisted of weighing 2 mg of sample in a tin crucible using a 6-digit analytical balance (Mettler Toledo). The crucible is dropped with an autosampler into the analysis chamber and is rapidly heated at ~1000 °C, in the presence of an oxidation catalyst and oxygen. This process allows the

Fig. 6. Nitrogen sorption properties at -196.2 °C for the mesoporous nanostructured silica particles: A) isotherms; B) BJH pore size distributions and C) cumulative pore volume based the NLDFT model.

organics to be completely decomposed into CO₂, H₂O and N₂. These gases were subsequently separated in a Porapak QS column at 80 °C and quantified with a TCD detector, using acetonitrile (99.9%) as external standard.

Inductively coupled plasma atomic emission spectroscopy analyses (ICP) were carried to determine the concentration of Fe in the optimal sample. The sample was dissolved in a 6 wt.% HF solution overnight to ensure complete dissolution. The liquid concentration was determined in an Optima 7000 DV Perkin–Elmer instrument.

TEM images were acquired on a Tecnai™ G2 F30 operated at 300 kV, equipped with a field emission gun, a Gatan bottom CCD 2 K × 2 K camera and an EDAX EDS detector. The sample was suspended in ethanol and then deposited onto a holey carbon grid until dryness.

The dynamic light scattering particle size (D_{DLS}) was measured using a Brookhaven Zeta-PALS analyzer, equipped with a 35 mW red diode laser, with a nominal 640 nm wavelength. The measurements were carried out on diluted ethanolic colloidal solutions by adding ~100 μL suspension into 10 mL of absolute ethanol. The laser angle for the measurements was set at 90° and a total of 10 runs were performed for each sample.

Silanol group density was evaluated according to equation (14):

$$\text{SiOH (wt.\%)} = \frac{2 \cdot \left(\Delta m^{\text{TGA}} - C \cdot \frac{320}{228} \right) \cdot MW_{\text{OH}}}{MW_{\text{H}_2\text{O}}} \quad (14)$$

Fig. 5. Time dependency of the hydrodynamic diameter for the MSN-Fopt on storage at room temperature.

Table 3Textural properties derived from N₂ physisorption at −196.2 °C.

Material	S _{BET} (m ² g ^{−1})	V _T (cm ³ g ^{−1})	φ _{BH} ⁱⁿ (nm)
MSN-D	75	0.431	Non porous
MSN-DC	763	1.293	2.6
MSN-Fopt	1073	1.523	3.1

where Δm^{TGA} is the TGA weight loss (wt.%) between 150 and 800 °C, C is the carbon wt.% determined from CHN analysis, 320 is the MW of CTAC while 228 is the carbon contribution per mole of CTAC, MW_{H₂O} is the molecular weight of water and MW_{OH} is the molecular weight of the hydroxyl.

3. Results

3.1. Fenton chemistry protocol. Detemplation and materials characterization

The MSN mesophase was prepared according to the method described by Möller et al. [18], using cetyltrimethylammonium chloride as template (CTAC). The amount of CTAC template present in the mesophase is *ca.* 80 wt.% as confirmed by TGA (Fig. 1-a). Fig. 1-b shows the DTGA pattern, which displays a single decomposition weight loss centred at 285 °C. The template decomposition is completed at 600 °C (Fig. 1-a).

Typically, a fraction of the suspension containing the native MSN was treated by a Fe^{III}/30% vol. H₂O₂ solution (20 mL, 7 ppm Fe). The detemplation conditions were optimized in terms of temperature

and time. Fig. 1-c shows that 90 °C reaction temperature gives rise to the highest template removal efficiency with a TGA residual weight loss of *ca.* 4.8 wt.%, compared to 9.8 wt.% at 70 °C and 27.1 wt.% at 30 °C. Reaction time was optimized as well at 90 °C (Fig. 1-d). After 3 h no significant changes were observed with TGA residues ranging 4.2–4.9 wt.%, which indicates that the detemplation at 90 °C is achieved relatively rapidly, within 3 h. Hence, optimal conditions were set at 90 °C and 3 h. The so-derived optimal material is hereafter denoted as MSN-Fopt.

The detemplation efficiency was corroborated by elemental carbon, showing a carbon concentration of 0.5 wt.% (Table 2), which corresponds to 99% removal efficiency compared to the mesophase (MSN-D, 55.6 wt.% C). This carbon-based residue content is equivalent to 0.7 wt.% CTAC, which would be left after detemplation. That means that the observed TGA weight loss of 4.4 wt.% is due to something else, and likely to the thermal surface dehydroxylation. Control experiments without Fe catalyst (Fig. 1) indicate that template removal occurs via non-Fenton H₂O₂ oxidation as well. It is however less efficient than the Fenton-based route at short reaction times, as evidenced by the higher TGA residues. Similar detemplation efficiencies by Fenton and H₂O₂ oxidation are only be obtained after 24 h.

The silanol concentration (Table 2) shows low residual Si–OH for the calcined material (1.1 wt.%) while the Fenton approach yields 7.1 wt.%, Therefore, the surface is highly hydroxylated. The large TGA weight loss discussed earlier can be then ascribed to dehydroxylation of the surface according to reaction (15):

Fig. 7. A) TGA in air of the mesophase decomposition; B) DTGA patterns, C) SAXS patterns of mesophase and calcined materials.

Table 4

Optimization of the calcination procedure after various work-ups. Materials properties: CTAC template content in the mesophases and textural properties derived from N₂ physisorption (–196.2 °C) of the corresponding calcined counterparts.

Material	CTAC (wt.%) ^a	S _{BET} (m ² g ^{–1}) ^b	V _T (cm ³ g ^{–1}) ^b
MSN-DC	80.2	763	1.293
MSN-CC	47.2	896	1.485
MSN-W1C	38.6	972	1.489
MSN-W2C	37.8	993	1.653
MSN-W3C	37.4	980	1.556

^a Weight percentage in the mesophase, determined from the TGA weight loss between 150 and 900 °C.

^b Textural parameters of the calcined mesophases.

This is also supported by former TGA-EGA studies that revealed a substantial H₂O release for a Fenton detemplated MCM-41 compared to the calcined counterpart [35].

The residual Fe content of the MSN-Fopt, coming from the Fenton medium and adsorbed on the sample surface, is 85 ppm (Table 2), compared to 200 ppm reported in a previous approach [35].

The structural ordering was studied by SAXS. The MSN-D mesophase shows a wormhole structure, displaying a 100-related reflection at 1.75° (Fig. 2). Calcination of the mesophase at 550 °C (MSN-DC) provokes structural shrinkage, which is visible in the shift towards higher angles (1.95°) of the 100-related reflection. Remarkably, the Fenton derived material, MSN-Fopt, does not show any structural shrinkage; the SAXS pattern virtually coincides to the mesophase, despite the fact that it was dried in an aqueous-based environment. This result is surprising when compared to our former study [35], which revealed a significant damage after drying in water. The absence of shrinkage for colloidal nanoparticles can be

explained as the drying of the nanoparticles is faster than for a bulkier MCM-41, due to the shorter channels length that imply less time under capillary stress.

Particle visualization by TEM (Fig. 3) did not evidence significant changes among the MSN-DC and MSN-Fopt in terms of morphology and degree of aggregation. Elongated particles, ranging 50–100 nm, with a relatively high degree of aggregation were observed. In case of MSN-Fopt, aggregation can be attributed to the drying itself since it is known that gels condense upon drying [37].

The hydrodynamic particle size was determined by dynamic light scattering (Fig. 4 and Table 2). The *D*_{DLS} for these types of MSN are larger than the sizes observed by TEM, which is consistent with former studies [18]. Comparison of the *D*_{DLS} parameters points out that calcination produces shrunk particles with hydrodynamic diameters of about 179 nm, as compared to the MSN-Fopt with 194 nm that is 8% larger, but comparable to the mesophase (196 nm). These results contrast to those reported by Kecht and Bein [36] that described a major particle agglomeration with *D*_{DLS} in the order of 500 nm after the Fenton oxidation, under ~460 ppm Fe, 20 °C for 18 h.

The stability of the colloidal MSN-Fopt was investigated by DLS measurements varying the storage time (Fig. 5). The particle size increases in 6% after 1 day of room temperature storage, which corresponds to a 0.25%·h^{–1} increase, and then it seems to be stabilized with a 16% increase after 6 days, corresponding to 0.11% h^{–1}.

Textural characterization by gas adsorption shows significant changes among the calcined and Fenton-derived materials. The isotherm of the calcined material (Fig. 6-A) is of type IV with two capillary condensation steps. The first one is located at 0.3 p/p₀ due to the intraparticle mesopores. This results in a sharp pore size distribution, associated to the internal pores centred at ca. 2.6 nm (Fig. 6-B). The second capillary condensation begins at 0.95 p/p₀

Fig. 8. TEM images (300 kV) of mesoporous silica nanoparticles: A) MSN-DC, B) MSN-CC and C) and MSN-W3C.

and this is due to the N_2 condensation in the extraparticle space. This is confirmed by the isotherm of the fully-templated mesophase, having the internal pores fully blocked by the CTAC template, which shows such a capillary rise. The narrow hysteresis indicates a good pore connectivity. The distribution of extraparticle pores is relatively wide which is associated to polydispersity of the particle sizes. The resulting textural parameters, $763 \text{ m}^2 \text{ g}^{-1}$ with $1.293 \text{ cm}^3 \text{ g}^{-1}$ (Table 3), are consistent with former studies when calcination was applied on a similar colloidal system [20]. The isotherm for the MSN-Fopt material is of type IV as well, with various differences compared to the calcined counterpart. The most remarkable feature is that the adsorption values are much higher in the complete p/p_0 range. Secondly, the first capillary condensation begins at higher p/p_0 due to the larger pores, centred at 3.1 nm (Fig. 6B). Both specific surface area and the total pore volume are higher than the calcined-based material with $1073 \text{ m}^2 \text{ g}^{-1}$ and $1.523 \text{ cm}^3 \text{ g}^{-1}$ (Table 3). The cumulative pore volume (Fig. 6-C) reveals that the larger pore volume for the MSN-Fopt mainly comes from the higher internal pore volume, with a difference between the materials of $0.31 \text{ cm}^3 \text{ g}^{-1}$ (measured at 5 nm). The difference of pore volume associated to the external porosity is much lower, with $0.05 \text{ cm}^3 \text{ g}^{-1}$, cf. 0.69 and $0.74 \text{ cm}^3 \text{ g}^{-1}$ (Fig. 6-C).

3.2. Optimization of the calcination protocol

Several work-ups were applied in order to reduce the amount of CTAC template, prior to calcination, and investigate its effect on the structural and textural properties. These were direct drying (MSN-D, fully containing the template), centrifugation-drying (MSN-C) and washing up to three times followed by drying (MSN-WXC series). Fig. 7-A shows the TGA patterns where one decomposition weight loss centred at 285°C is visible for all mesophases (Fig. 7-B). The amount of template was substantially reduced after the various work-ups (Table 4). The mesophase contains *ca.* $80 \text{ wt.}\%$, that was diminished after centrifugation, resulting in $47 \text{ wt.}\%$. This corresponds with a 41% reduction with respect to the mesophase. Application of several washing steps gives rise to further CTAC removal; the first washing reduces the template by 52% ($39 \text{ wt.}\%$), while the second and third hardly decrease the template content. Hence the first wash produces the largest CTAC reduction.

The SAXS patterns of these mesophases show a worm-hole structure, which characteristically displays a 100-related reflection. In all the cases the reflection appears at 1.75° (for the sake of clarity one pattern is shown in Fig. 7-C). Calcination of the mesophases at 550°C gives rise to the total elimination of CTAC and a certain degree of structural shrinkage, which is visible in the shift towards higher angles of the 100-related reflection in the SAXS pattern. For all the mesophases, shrinkage was nearly identical with a shift from 1.75° up to 1.95° (Fig. 7-C).

Particle visualization by TEM did not evidence significant changes among the calcined samples in terms of morphology and degree of aggregation; in all cases elongated particles with a relatively high degree of aggregation are observed (Fig. 8).

The textural properties determined by gas adsorption show however significant variations among the calcined mesophases. The isotherms and PSDs (Fig. 9-A,B) are characteristics of the type IV with two capillary condensation steps, with similar features as those discussed previously for MSN-DC (Fig. 6). The specific surface area increases notably along the series from 763 up to $993 \text{ m}^2 \text{ g}^{-1}$ for the optimal material (Table 4). The same occurs with the total pore volume with an increase from 1.293 to $1.653 \text{ cm}^3 \text{ g}^{-1}$. The cumulative pore volume (Fig. 9-C) evidences that the increase of the total pore volume originates from the higher intraparticle

Fig. 9. Nitrogen sorption properties at -196.2°C for the mesoporous silica nanoparticles: A) isotherms; B) BJH pore size distributions and C) cumulative pore volume based the NLDFT model.

Fig. 10. Specific surface area and pore volume of the activated materials as a function of the mesophases template content (CTAC). Calcined-based materials: a) MSN-DC, b) MSN-DC, c) MSN-W1C, d) MSN-W2C, e) MSN-W3C; and Fenton detemplated: f) MSN-Fopt. The line connects the calcined-based materials.

volume, rather than the extraparticle texture. This implies that the particle morphology and size are not affected as much as the internal pores.

4. Discussion

From the optimization study, it appears that the textural properties of calcined materials are enhanced with the washing protocol. In order to shed light on this, a correlation between the textural parameters and the amount of CTAC was investigated. Fig. 10 represents the specific surface area and pore volume as a function of the CTAC template content that is burnt during the calcination step. Clear decreasing trend lines were found. The correlations demonstrate that both specific surface area and pore volume can be enhanced when the CTAC concentration is lowered by washing, with a maximum increase of 30% in both parameters. Therefore, the optimal calcination protocol (W2C), enhances the surface area notably compared to the direct calcination route (DC). This effect could be explained by the exothermal and hydrothermal conditions during the CTAC burning inside the pores. Alkyltrimethylammonium surfactant-based MCM materials typically decompose via Hofmann degradation at low temperatures, followed by sharp exothermal oxidation at 350 °C [38]. Having a larger fraction of template (DC > CC > W-samples) implies that hot-spots may occur leading to severe loss of the internal textural features. Such differences in texture may be ascribed to differences in the densification of the material, leading to reduced specific textural parameters. This is consistent with the reduction of the textural parameters of gels upon calcination, due to the increased skeletal density [39].

The single-step Fenton-based detemplation (*Fopt*) gives rise however, to the highest surface area (Fig. 10). The pore volume remains the typical value reported for the washing-calcination-based protocol. The properties of the *Fopt* can be explained by the milder conditions applied in the Fenton protocol. This is illustrated in Fig. 11 where calcination is compared to the optimal Fenton protocol. In both cases, the final decomposition products are $\text{CO}_2 + \text{H}_2\text{O}$, but the applied conditions differ substantially. Mechanistically, under the Fenton-route silanol condensation reactions are nearly negligible, or much slower, as compared to the calcination route. Under calcination, shrinkage is believed to occur by thermal dehydroxylation and formation of siloxane bonds (Fig. 12). This means that under non-thermal Fenton-reaction conditions, no shrinkage is expected and consequently the pore size is expected to be bigger as was already shown (Fig. 6). No capillary stress-induced shrinkage was observed, and this was interpreted by the relatively faster drying of nano-scale MSN particles, compared to a bulky

Fig. 12. Representation showing the shrinkage of the structure. Silanol groups combine and new siloxane bonds are formed, resulting in shrinkage.

micro-sized MCM-41 [35]. The mild conditions, in temperature and time, also explain a limitation in surface condensation reactions, implying that the surface is highly hydroxylated. However, such high degree of hydroxylation may give rise, after prolonged time, to condensation between adjacent silanols of different particles, giving rise to a particle size increase. But the particle size increase can also be explained by a pore-expansion effect that typically occurs under hydrothermal conditions of ordered MCM-41 type mesoporous materials [40]. This is further clarified with the stability test at room temperature (Fig. 5), estimated by the particle size increase; the stability is a good indication that the rate of condensation/pore expansion is moderately slow.

Explaining the higher surface area is not straightforward, because smaller pores as was found for the calcined case, should give higher surface areas; but the opposite trend was found. There are several additional aspects that may explain that. One reason can be the possibility of having occluded pores, as was demonstrated for the SBA-15 [41]. However, the N_2 isotherms do not show any indications of pore restrictions. The other, and most likely explanation has to do with differences in density. The calcined material is expected to have a higher density, meaning that there is less volume (and less particles) per gram, thus contributing less to the surface area and pore volume.

Fig. 11. Schematic model summarizing the relation between the detemplation conditions and the derived materials properties, for the studied MSN.

5. Conclusions

Calcination of colloidal silica nanoparticle precursors can be optimized in terms of the resulting material textural features; the repeatedly washing of the CTAC template removes about 50% of the template, and this enhances the surface area and pore volume by 30% after applying calcination.

A single-step Fenton chemistry-based detemplation protocol applied to fresh colloidal nanoparticles produces particles without structural shrinkage. About 99% of the template is removed and the pore volume and specific surface area are enhanced, leading to the highest specific surface area and no particle aggregation. The colloidal particles are relatively stable during storage at room temperature, implying that pore expansion or condensation reactions, or both, are slow, with an increase in the particle size of 16% in 6 days. The residual Fe in the resulting solid was as low as 85 ppm in the solid, which is beneficial for potential applications. Overall, the enhanced properties, *i.e.* no shrinkage, bigger pores, highly hydroxylated surface, can be ascribed to the milder applied conditions. The higher specific surface area is also ascribed to the mild conditions, but it is less obvious; it is ascribed to the lower skeletal density, which is typically high when calcination is applied due to the structural densification.

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