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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 Fe^{3+}/Fe^{2+} cycle that is used as catalyst and H_2O_2 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 $0.11\% \cdot h^{-1}$, has been determined.

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)-ethenylene [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 $OH^{\bullet}$ radicals following this redox cycle:

$$H_2O_2 + Fe^{3+} \rightarrow HO_2^{\bullet} + H^+ + Fe^{2+} \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^- + Fe^{3+} \quad (2)$$

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

$$MSN(CTAC) + nOH^{\bullet} \rightarrow MSN(\ ) + xCO_2 + yH_2O \quad (3)$$

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

De Laat and Le reported that reactions involving halogen radicals occur and are much faster than $OH^{\bullet}$ radicals [34]. As the CTAC template (cetyltrimethylammonium chloride) employed in this study contains Cl^-, this can also be oxidized to form dichloride anion radicals, $Cl_2^{\bullet -}$ (4)–(6):

$$Cl^- + OH^{\bullet} \rightarrow ClOH^{\bullet -} \quad (4)$$

$$ClOH^{\bullet -} + H^+ \rightarrow Cl^{\bullet} + H_2O \quad (5)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -} \quad (6)$$

It was demonstrated that in the presence of Cl^-, the dichloride anion radicals ($Cl_2^{\bullet -}$) are the dominating oxidizing species [34]. Therefore the following oxidative pathway is also considered (7):

$$MSN(CTAC) + n'Cl_2^{\bullet -} \rightarrow MSN(\ ) + x'CO_2 + y'H_2O + z'Cl^- \quad (7)$$

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:

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \quad (8)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (9)$$

$$R^{\bullet} + OH^{\bullet} \rightarrow ROH \quad (10)$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + OH^{\bullet} \quad (11)$$

$$HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \quad (12)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (13)$$

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, $Si(OC_2H_5)_4$, 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-F*opt*	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}