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“Liquid-Phase Calcination” of Colloidal Mesoporous Silica Nanoparticles in High-Boiling Solvents

Valentina Cauda,[†,‡] Christian Argyo,[†] Davin G. Piercey,[†] and Thomas Bein*[,†]

[†]Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstrasse 5-13 (E), 81377 Munich, Germany

[‡]Italian Institute of Technology (IIT), C.so Trento 21, 10129 Turin, Italy

Supporting Information

ABSTRACT: We report on a novel high temperature liquid phase “calcination” method with trioctylphosphine oxide (TOPO), tri-*n*-octylamine (TOA), and squalene for removing the template and strengthening the silica network in colloidal mesoporous silica (CMS) nanoparticles. For such materials, the common calcination procedure in air would result in strong agglomeration, thus preventing their use in colloidal suspensions. The highest efficiency of the new approach is obtained by thermal calcination in TOPO at only 275 °C, as shown by an increasing degree of silica condensation, and the retention of the high colloidal stability of the CMS nanoparticles. Moreover, we also show the ability of the TOPO treatment to remove the template, thus saving a preparation step. The resulting CMS nanoparticles retain the ordered mesostructure, high porosity, and large surface area of the original mesoporous nanoparticles, while showing a much greater degree of silica condensation and high stability. The concept of “liquid calcination” represents a powerful general approach for the preparation of stable colloidal porous nanoparticles.

Colloidal mesoporous silica (CMS) is of great interest[1] for its unique properties regarding catalysis, separation, chemical sensing, and drug delivery.

The defining factor of the synthesis of mesoporous silica is the use of a templating surfactant causing self-assembly of the material at mild temperatures. The subsequent removal of this template is the key step for obtaining accessible mesopores, large surface areas, and pore volumes.[2] Established methods of template removal include calcination in air, extraction in ethanol with various solutes, microwave irradiation, and UV light.[3] However, all these methods except the solution-phase ethanol-based template extraction are conducted in the solid phase, which is appropriate for bulk mesoporous silica or for particles with a size far greater than 100 nm.[4] During calcination, condensation of silanol groups (Si−OH) into siloxane (Si−O−Si) bridges takes place, thus consolidating the mesoporous structure.[5] However, when CMS nanoparticles (e.g., 20−100 nm in size) are calcined, strong aggregation prevents their subsequent redispersion as isolated nanoparticles in a colloidal solution. For this reason only solvent extraction, hydrogen peroxide oxidation, or dialysis can be applied,[6] but no further condensation of the silica network after the room temperature sol−gel synthesis is obtained. This implies the low stability of the extracted CMS particles in aqueous media, which can pose a serious impediment for applications such as drug delivery. We have previously shown that the silanol groups are the point of initial attack and silica degradation, leading to rapid particle destruction in simulated biological fluids.[7] Current attempts at increasing the stability of CMS in biological media have mainly involved polymeric-shell functionalization of the outer particle surface.[8]

Here we present for the first time the use of a liquid-phase high-temperature “calcination” of CMS nanoparticles in high boiling point organic solvents (HBS), leading to significant silica condensation and also to template removal. Trioctylphosphine oxide (TOPO), known for its stabilizing effect in nanoparticle and quantum dot synthesis,[9] was used as solvent for high temperature treatment of the CMS, in both thermal and microwave-assisted liquid calcination. In addition we have examined two other HBS, tri-*n*-octylamine (TOA, $C_{24}H_{51}N$) and squalene ($C_{30}H_{50}$).[10]

The CMS nanoparticle synthesis (sample **UN-CMS**) was carried out as previously reported[11] (see Supporting Information (SI) for experimental details). The ability of the HBS treatment to enhance the degree of silica condensation in the already template-extracted CMS nanoparticles (sample **ex-CMS**) was examined with thermal liquid calcination at 400 °C in squalene (sample **LC-1**), TOA (sample **LC-2**), and TOPO (sample **LC-3**), in this last case also at 275 °C (sample **LC-4**), for 5 h under a N_2 atmosphere. Moreover, we have combined the ability of the TOPO treatment to enhance silica condensation with the removal of the template phase in as-synthesized CMS nanoparticles (template: cetyltrimethylammonium chloride (CTAC)). This was achieved in a thermal liquid calcination at both 275 °C (sample **LC-5**) and 400 °C (sample **LC-6**) on **UN-CMS** nanoparticles.

Microwave (MW) heating has been demonstrated to enhance reaction rates, selectivity, and product yields in chemical synthesis.[12] Due to its polarity, TOPO can couple with microwaves and efficiently convert electromagnetic energy into heat, resulting in rapid heating of the bulk solution. TOPO microwave-assisted liquid calcination was carried out at 200 °C for 30 min (sample **LC-7**) or 2 h (sample **LC-8**) with template-extracted CMS nanoparticles (**ex-CMS**). All TOPO-calcined samples were thoroughly washed.

The degree of condensation of the silica network in the as-synthesized (**UN-CMS**) and template-extracted CMS nanoparticles

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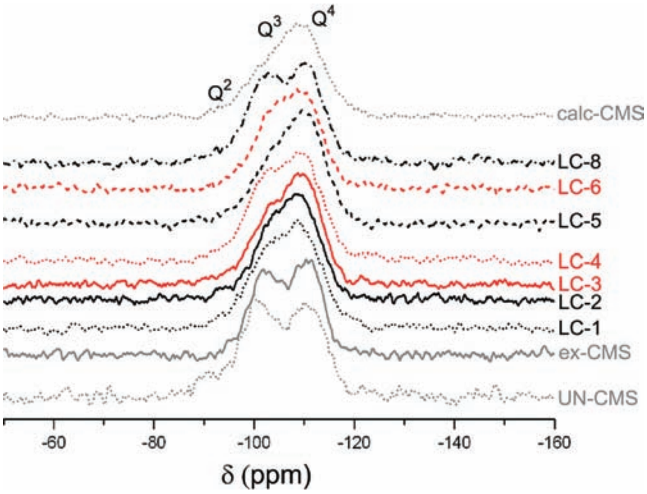

Figure 1. ^{29}Si-MAS NMR spectra of the as-synthesized (**UN-CMS**), template-extracted (**ex-CMS**), and air-calcined (**calc-CMS**) CMS nanoparticles and the liquid-phase-calcined CMS nanoparticles with squalene (**LC-1**), TOA (**LC-2**), and TOPO (from **LC-3** to **LC-8**).

Table 1. Quantification of the Integrated Area of Q^3 and Q^4 Peaks and Their Relative Change upon Thermal Treatment

Sample	Treatment	Q^3/Q^4 ratio	Increase of condensation[a] (%)
UN-CMS	-	1.08	-
ex-CMS	EtOH@78 °C	1.02	+5.56
LC-1	Sqa@400 °C	0.755	+30.1
LC-2	TOA@400 °C	0.795	+26.2
LC-3	TOPO@400 °C	0.816	+24.5
LC-4	TOPO@275 °C	0.801	+25.8
LC-5	TOPO@275 °C	1.04	+2.78
LC-6	TOPO@400 °C	0.910	+15.7
LC-8	TOPO@200 °C MW	1.01	+6.48
calc-CMS	550 °C (air)	0.549	+49.2

[a] Based on the decrease in % of the Q^3/Q^4 ratio of each sample with respect to the reference one (**UN-CMS**).

(**ex-CMS**) is strongly enhanced by all the liquid-phase calcinations treatments, as observed by ^{29}Si-MAS NMR spectroscopy (Figure 1). Quantification of the integrated area of the Q^n peaks is given in Table 1 and in the SI, clearly indicating a strengthening of the silica network due to the HBS calcination treatments. Specifically, a consistent increase of the Q^4 peak at −110 ppm [Q^n = Si(OSi)$_n$(OH)$_{4-n}$ with n = 2−4, 4 representing the fully condensed silica] upon "liquid calcination" is observed with respect to the Q^3 peak at −102 ppm (silica with one terminal hydroxyl group) in all HBS-calcined samples, except the MW-treated ones (only **LC-8** is reported in Figure 1). We attribute the lower efficiency of the MW treatment to both its lower temperature (200 °C) and shorter time (2 h). For the two TOPO-calcined samples at 275 (sample **LC-4**) and 400 °C (**LC-3**), a similar Q^3/Q^4 ratio is obtained, thus indicating that no further increase of silica condensation is obtained above 275 °C. The highest Q^4 fraction, implying the highest degree of silica condensation, was obtained upon calcination in squalene (**LC-1**). Air calcination at a still higher temperature (550 °C) can lead to an even higher degree of condensation (sample **calc-CMS**); however, such a sample cannot be dispersed again as colloidal solution.

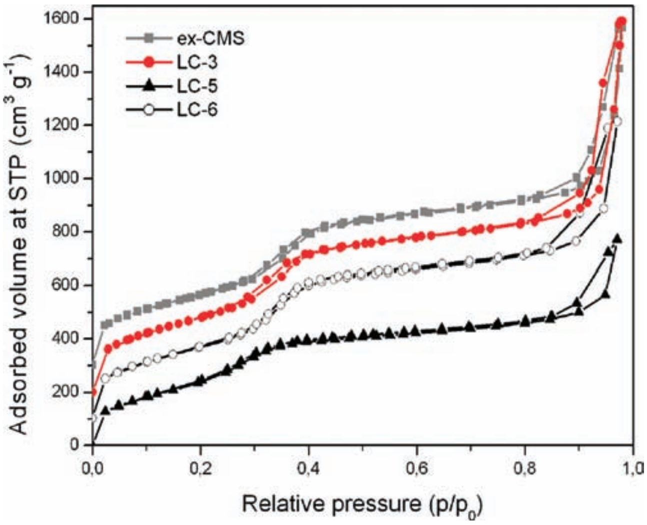

Figure 2. Nitrogen sorption isotherms of the unextracted/TOPO-calcined CMS nanoparticles (**LC-5** and **LC-6**), compared to the template-extracted CMS (**ex-CMS**) and extracted/TOPO-calcined CMS (**LC-3**). The curves are shifted by 100 units each.

Dynamic Light Scattering (DLS, Figure S-1 in the SI) shows that the colloidal stability in ethanol of all the CMS nanoparticles is not affected after high-temperature treatment with HBS, and particle sizes do not change significantly as a result of different solvents and thermal treatments. As previously mentioned, air-calcined CMS nanoparticles are no longer able to form colloidal solutions. All the HBS-treated samples do not show any structural difference by X-ray diffraction; in particular no shift of the (100)-like reflection to higher angles is observed (Figure S-2.c). This indicates the absence of the unit cell shrinkage, in contrast to conventional air-calcined CMS (Figure S-2.c).[13] Complete removal of TOPO by repetitive washing was confirmed by IR spectroscopy, whereas residual squalene and TOA are still present in both samples **LC-1** and **LC-2** (Figures S-2 and S-3 in the SI.). For this reason, the use of TOPO solvent is preferred with respect to squalene and TOA, even if the degree of silica condensation shown by ^{29}Si-MAS NMR is slightly lower with TOPO treatments.

The enhancement of silica condensation in combination with the template extraction ability of the TOPO treatment was investigated with the unextracted CMS nanoparticles (**UN-CMS**), using the thermal calcination method. Indeed, the resulting sample **LC-6** shows a strengthening of the silica network in ^{29}Si-MAS NMR spectroscopy (Figure 1 and Table 1) and good colloidal stability in ethanolic solution with a homogeneous particle size distribution (Figure S-1). TGA and IR spectroscopy show almost complete removal of the template (see Figure S-6). The corresponding nitrogen sorption measurements (Figure 2) demonstrate that calcining unextracted CMS particles in TOPO at 400 °C is as efficient as the solution-phase ethanol extraction method (see Table 2). However, calcination of the unextracted CMS in TOPO at 275 °C (**LC-5**) is not sufficient to completely remove the template and to enhance the silica condensation as in the sample treated at 400 °C (**LC-6**).

Table 2. Characterization of the Samples before and after HBS "Liquid-Calcination" Treatments

Sample	BET surface area ($m^2\ g^{-1}$)	Pore volume[a] ($cm^3\ g^{-1}$)	DFT pore diameter[b] (nm)	DLS particle size[b] (nm)
ex-CMS	978	0.78	3.9	59
LC-1	918	0.71	3.5	51
LC-2	968	0.76	3.8	59
LC-3	1032	0.78	3.9	91
LC-4	1052	0.80	3.9	106
LC-5	928	0.60	3.5	68
LC-6	998	0.77	3.9	106
LC-7	850	0.75	3.9	59
LC-8	1087	0.83	3.8	106

[a] Pore volume was calculated only up to a pore size of 8 nm to remove the contribution of textural porosity. [b] Referred to the peak value of the size distribution.

HBS-calcined CMS samples also exhibit a comparable porosity. The N_2 sorption isotherms of the other HBS-treated samples are reported in the SI; see also Table 2.

Summarizing, we describe a novel "liquid calcination" method for preparing highly condensed mesoporous silica nanoparticles that form stable colloidal suspensions. The CMS nanoparticles calcined in high-boiling solvents (HBS) retain their original pore size, experience no unit cell shrinkage or particle agglomeration, and exhibit a significant decrease in silanol content. The high degree of condensation and the resulting stability will open up new fields of application for colloidal mesoporous nanoparticles.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed CMS nanoparticle synthesis, template extraction, thermal and microwave-assisted calcination, and further characterization results (N_2 sorption, TEM, XRD, IR spectroscopy, TGA, ssNMR). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

bein@lmu.de

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