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Bruno Chal, Lucian Roiban, Karine Masenelli-Varlot, Guilhem P. Baeza, Bernard Yrieix, et al.: 3D multi-scale quantification of industrially relevant ultra-porous silicas by low-dose electron tomography combined with SANS. Journal of Non-Crystalline Solids, 2021, 557, 10.1016/j.jnoncrysol.2020.120577 . hal-03484850

HAL Id: hal-03484850 https://hal.science/hal-03484850

Submitted on 10 Mar 2023

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0022309320306876 Manuscript_0084d71cd35edd3c1c7474ef10f5b1b2

3D multi-scale quantification of industrially relevant ultra-porous silica by low-dose electron tomography combined with SANS

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Abstract: Due to their versatile properties, nanostructured silicas are used in numerous applications for which structural properties are decisive. Being able to thoroughly understand porous multi-scale structures is therefore a means of improving composites and ensuring their fast processing and their durability. In this framework, electron tomography (ET) is a convenient tool that permits analysing the inner structure of any nano-object made of particles, necks, aggregates and pores. However, some materials are very sensitive to the electron beam, which can lead to misinterpretation. In this article, we highlight how any fractal silica, whether precipitated, fumed or in aerogel form, can be effectively characterized and described. Step-by-step low-dose tomography allows the unprecedented visualisation and quantification of architectures on large volumes, essential to feed numerical simulations. This local analysis is strengthened by statistical observation provided by Small Angle Neutron Scattering (SANS). We finally show how this kind of work can benefit an ageing study. **Keywords**: Porous material, Multi-scale structure, Electron Tomography, SANS, silica, aerogel

Highlights: Careless TEM imaging on silica induces greater pore sizes and misinterpretation of the aggregates morphology.

Low-dose TEM enables accurate 3D Particles/Pores/Neck multi-scale anisotropic structures imaging.

Electron Tomography shades light on pattern-less structure, within large aggregates.

Ageing is evidenced at the particle, neck and aggregates lengthscales with SANS and Electron Tomography.

Graphical abstract:



1. Introduction

Fractal silicas are relevant materials at the industrial scale for basic applications (toothpaste), high-technology composites (tires) and breakthrough innovations (living on Mars). Nanostructured silicas are obtained either by wet (precipitated, aerogel) or dry (fumed) processes. Due to their origin, they exhibit different structural and chemical properties. In wet synthesis [1–3], precursor molecules such as alkoxides of the Si(OR)₄ type (TEOS [4], TMOS [5], PEDS [6], etc.) or water glass (sodium silicate Na₂SiO₃) [7,8] are used. Polymerisation occurs via hydrolysis and condensation reactions, mostly in an organic solvent. Macromolecules and then particles of silica, connected to each other by necks, are formed. Depending on the parameters used during synthesis (molar ratio, temperature, time, etc.), growth or connection is favoured. In the case of precipitated silica, growth is promoted before aggregation. On the contrary, aerogels are based on a network with a smaller primary particle size. In both cases, synthesis can include a hydrophobisation step, which is often the case regarding silica aerogels [9–11]. Fumed silica is obtained by the combustion of SiF₄ or SiCl₄ in O₂/H₂ flames (1200-1500°C) [12–14]. According to the flame temperature or the cooling step, several structural (specific surface area, particle size, etc.) and chemical (silanol groups, SiOH; siloxane bridges, SiOSi) properties can be obtained [15-17]. Nanostructured silicas have high specific surface areas (50-1000 m².g⁻¹ and considerable porosity (> 80%) [18]. They are used in numerous applications [19,20], for which structural properties are decisive: tires (reinforcement) [21], paints (thickeners [22]), insulation (core material) [23-25], drug delivery [26], particle collectors [27], antireflective nanocoatings [28] and so forth. Their chemical properties are also important as they often determine processability [29] and durability [30]. Structural analysis is important in order to understand how silica plays a role in applications and enables properties tuning to fulfil specific requirements. Moreover, core assessment provides valuable information for simulation and prediction works [31–37].

Amorphous silica has already been analysed by TEM, focusing mainly on aerogels [38–41], and fumed [42] and precipitated [43] silicas. However, this material appears to be highly sensitive to the electron beam. Thus, the samples can be damaged if the TEM analyses are performed without taking particular care [43] and they can lead to the misinterpretation of structural properties (particle size, pore size, aggregate size, connectivity, etc.), and thus false thermal and mechanical simulations [44,45]. Therefore, the use of electron tomography on silicas, which requires longer exposure to the electron beam, as well as stability during acquisition, has been very limited up to now [46–48]. Electron tomography [49–51] consists in using a TEM to acquire a series of projections through different angles, knowns as tilt series. Using a mathematical algorithm [52], the volume is reconstructed by re-projecting the tilt series. Then, the segmentation, made by selecting the grey levels of interest, is used to generate a 3D model that allows 3D quantification of morphological parameters such as the porous structure, the silica grain size, networks of pore connection, etc. In recent years, this advanced technique has been adapted to satisfy the requirements of beam sensitive materials [53]. In addition to silica, biological samples [54] and polymer-based materials [55] are examples of beam-sensitive materials, for which low-dose or cryo-techniques are common [56,57]. One way of overcoming the problem is to lower the electron dose, a means employed in this work, with improved step-by-step fast-image recording for electron tomography in bright field mode, exemplified in reference [58].

In this article, in good agreement with a recently developed methodology [48], we combined local characterisation tools (TEM, electron tomography) and statistical characterisation tools (SANS) to reliably retrieve the structural properties of 3D silica. We performed this characterisation on industrially relevant silicas of different natures: precipitated, fumed and aerogel silicas, and discuss the main differences between those fractal materials. They cover a wide range of pore/skeleton textures of interest to obtain functional properties.

2. Methods

2.1. Materials

Three silicas were selected among industrially relevant products and are named hereafter: precipitated, fumed and aerogel. The precipitated silica was Tixosil 43 from Solvay (France) with a given tape density of 0.05 g.cm⁻³ and a specific surface area of $250 \text{ m}^2.\text{g}^{-1}$. The fumed silica was Konasil 200 from OCI (Korea) with a given tape density of 0.15 g.cm⁻³ and a specific surface area of $200\pm25 \text{ m}^2.\text{g}^{-1}$. The aerogel was Isogel granules from Enersens (France), with a given tape density of 0.075 g.cm⁻³ and a specific surface area of $850\pm25 \text{ m}^2.\text{g}^{-1}$. The specific surface areas were also determined experimentally using sorption nitrogen measurements: precipitated: 255 m².g⁻¹; fumed: $205 \text{ m}^2.\text{g}^{-1}$; aerogel: $830 \text{ m}^2.\text{g}^{-1}$.

2.2. Transmission electron microscopy

Transmission electron microscopy (TEM) analysis and electron tomography (ET) were performed on an FEI E-TEM TITAN (80 keV-300 keV) electron microscope operating under high vacuum. The microscope is equipped with the OneView camera from Gatan ($4k \times 4k$ resolution) and the experiments were performed in bright field mode. Because the samples had a low contrast during the experiment, an objective aperture of 40 µm was used to enhance the contrast.

As silicas have high specific surface areas and complex surface chemistries involving hydrophilic silanol groups, they can evolve due to exposure to water or ethanol [1,59]. In order to minimize the influence of the preparation step, we used a dry procedure. A small amount of silica was placed in an agate mortar and crushed in the case of the aerogel (1 macroscopic granule). The powder was then captured manually with a 300-mesh (ca. 50 μ m) copper grid covered with a holey carbon film. To do this, the grid, handled using tweezers, was used as a sieve and passed through the pile of powder, then taped at the edge of the mortar.

TEM imaging of a beam sensitive silica

In Figure 1, we present a single object of the fumed silica K200. Micrograph (a) was captured with precautions taken regarding the dose. Micrograph (b) exhibits the consequences of an uncontrolled exposure to the electron beam.

Figure 1: TEM micrograph of (a) the fumed silica acquired with a dose equal to 14 e⁻.Å⁻² (b) The same object observed with a much higher dose to achieve a good signal-to-noise ratio. The numbers correspond to pores that have evolved due to over-exposure: (1) + (2) \rightarrow (3). The arrow indicates a 200 nm long particle arm displaced due to over exposure. The focus change is due to the displacement of the sample under the electron beam.

Due to the speed of evolution in the case of inattention, it is not possible to know whether the beam modified micrograph (b). However, the comparison unambiguously shows that the silica has been altered at several length scales. In particular, the arms or necklaces, formed by the succession of primary particles, have been displaced (see arrow in (b)). The electron beam also redefined the porosity observed in transmission (see numbers). Imaging structures is a topic on its own, but having reliable quantitative data to feed simulation models is also primordial [32].

After selecting an object at low magnification, a common way to acquire TEM micrographs of beam-sensitive materials is to adjust the parameters outside the region of interest. Afterwards, the electron beam is displaced to the desired object which is instantly captured. High magnification acquisitions are not always suitable as they are associated with considerable electron rate. In this case, we think that it is better to lose a little contrast than to modify the sample. To enhance the contrast an objective aperture can be used, as was mentioned previously in section 2.2. Our silica micrographs are acquired with all these precautions.

2.3. Electron Tomography (ET)

The sample preparation was similar to the one used for standard TEM observations (dry procedure described above), but 200-mesh (ca. 75 μ m) grids were used. Moreover, gold nanoparticles (BBI Solutions – 5 nm) were deposited beforehand on the microscopy grid. They were used as fiducial markers for the alignment step. A Fischione high tilt holder was used.

Low-dose step-by-step fast tomography was performed [60], with a 2° angle increment, allowing the acquisition of a tilt series (75 images) in around 120 seconds.

Image recording was semi-automatic, using a Digital Micrograph plugin developed in-house. The pixel size ranged between 0.16 nm and 0.33 nm, and was situated in the fair range to perform quantification on phases as small as 3nm in size. Image alignment was performed using the Imod software [61]. The reconstruction was done using 15 iterations of the ART algorithm [62] implemented via TomoJ [63] and ImageJ. Segmentation and quantification were performed with different tools from ImageJ [64,65] and 3D Slicer [66].

Electron Tomography (ET) on a beam-sensitive silica.

Figure 2: Fumed silica exposed to an electron dose rate of 28 e^{-} . Å^{-2} . s^{-1} : (a) Initial, (b) after 200 s, (c) after 450 s. The continuous film up to 450 seconds is available in SI 1. Images were denoised using a Gaussian blur filter (radius: 2 pixels – pixel size = 0.2 nm). (d) is a merge channel of images a-c), i.e. the overlapping of the three images. The white arrow in a-c points toward a region, among others, that was displaced.

Performing electron tomography with a beam sensitive sample is more difficult than just taking a micrograph, as the beam is applied for a significantly longer time. An alteration of the sample would be detrimental for at least two reasons: (i) the sample is no longer representative of the native material; (ii) the differences between the beginning and the end of the tilt series introduce uncertainties during the reconstruction.

In supplementary information (SI 1), we provide a movie of an agglomerate of the fumed silica K200, acquired with an electron flux of 28 e⁻. Å⁻².s⁻¹. Shrinkage of the silica aggregates as irradiation occurs is evidenced by micrographs extracted from this movie in Figure 2. This enabled us to visually define a critical dose from which irreversible damage occurs: 4200 ± 600 e⁻. Å⁻². With this knowledge, we were then able to select the dose rate to safely acquire a full tilt series (70 micrographs), knowing that the sample was exposed to the electron beam flux for 120 seconds in fast step-by-step tomography. Regarding this silica, we selected a dose rate of 6 e⁻. Å⁻².s⁻¹, leading to a total dose of 740 e⁻. Å⁻².

2.4.Small Angle Neutron Scattering

SANS experiments were performed at LLB (Laboratoire Léon Brillouin, CEA Saclay, France) on the beam-line PA.20 (G5-1). Collimation is rectangular with a typical beam size of 1 cm². Three configurations were used to measure the scattering intensity I(q) with scattering vector q from 7.85 10⁻³ nm⁻¹ to 3.75 nm⁻¹. (i) Small Angles with a wavelength of $\lambda = 15$ Å and a sample-detector distance of 18.45 m, (ii) Intermediate Angles with a wavelength of $\lambda = 6$ Å and a sample-detector distance of 8 m, and (iii) Large Angles with a beam wavelength of $\lambda = 4$ Å and a sample-detector distance of 1.5 m. Scattering intensities acquired in the Intermediate Angle configurations are in absolute units (cm⁻¹) (Water as calibration standard, and the thickness and transmission of samples were considered). Scattering intensities I(q) collected from the two other configurations were treated to match the Intermediate Angle results. In the regions where data overlapped, points with the highest signal-to-noise ratio were kept. Data treatment was done using the PASINET program developed at LLB. The incoherent scattering background was subtracted by iteration in order to obtain the best linearity (least square regression algorithm) at low scattering vector q in a log/log representation.

Precipitated and fumed silica samples being cohesive materials; they were pelletshaped (100 mg – 1 mm thick) using a Zwick Roell press. Oedometric compression was performed at 0.6 MPa with a relaxation step of 30 minutes. Loading and unloading were performed at 1 and 0.1 mm.min⁻¹ respectively to ensure a flat surface. Silica aerogels are large granules with no cohesion. They were therefore slightly packed inside a metal O-ring sandwiched between two Kapton films. Acquisitions with only two Kapton films were performed to subtract the corresponding scattering intensity. In every case, the volume fraction of silica was determined from the geometrical volume of the sample and the powder mass, and then used to normalize the data.

2.5. Nitrogen sorption

Nitrogen sorption measurements were performed on a Bel Sorp Max apparatus from Bel Japan Inc. The mass of sample analysed ranged from 40 to 100 mg, depending on the specific surface area of the material. A pre-treatment of 2 hours at 140°C under vacuum (10 Pa) was performed to retrieve physiosorbed species (mainly water) from the surface. Acquisition was done at 77.4 K. Data were acquired during sorption and desorption with a partial vapour pressure ranging from 0 to 0.997 p₀, where p₀ is the equilibrium vapor pressure of nitrogen at 77.4 K. The condition of going from one point to the next one was that the pressure did not vary more than 0.3% in a 300second window. The specific surface area was extracted from the BET method [67] (with an adsorption cross-section of 0.162 nm²) and the pore size distribution was retrieved from the BJH analysis on the desorption branches [68].

3. Results and discussion

3.1. Introduction on structural properties

The description follows an increasing degree of complexity regarding the surface chemistry. A precipitated silica is mainly covered with silanol groups, Si-OH. A fumed silica is mainly covered with siloxane bridges, Si-O-Si, and with some rather isolated silanol groups. Finally, a silica aerogel reveals a complex chemistry including both functions already mentioned, but also intentionally placed hydrophobic groups, Si-OCH₃. In this section, we first present local observations using TEM (Figure 3), then move to the statistical results obtained with SANS (Figure 4).

In Figure 3a-c we present electron micrographs of a precipitated silica agglomerate captured by BF-TEM consisting of a nest of connected particles with a few transverse pores. In micrograph 3a, the agglomerate observed has a size of about 1 μ m, but statistical analysis on this kind of object shows a large dispersion in size related to the uneven dispersion resulting from the dry procedure used to prepare the samples. There is no doubt that this rather dense object is the assembly of several agglomerates. Figure 3b and c are micrographs of the same silica, obtained at higher magnifications. Figure 3b highlights inter-agglomerate pores, with one measured at about 70 nm (projection in transmission). At a lower length scale, we can observe in Figure 3c how aggregates assemble, forming pores of smaller sizes, with one measured at around 20 nm. Figure 3c further allows the observation of primary particles, which are spherical in shape. To incorporate some statistics, we conducted

an analysis focusing on the primary particles from several objects of the precipitated silica. Based on 30 measures, the mean particle diameter associated with this analysis is 15.0 nm with a standard deviation of 4.1 nm.

Figure 3: TEM micrographs of fractal silicas observed at three length scales. a-c) Precipitated; d-f) Fumed. g-i) Aerogel. Black dots are gold nanoparticles used to align images before tomography reconstruction. Blue refers to the primary length scale of the particles (thickness), while yellow is associated with pores. The size of the elements indicated is displayed in white.

Figure 3d-f are micrographs obtained from the fumed silica, a fibrillar flat assembly of particles with numerous transverse pores. The agglomerate shown in Figure 3d is less dense than the objects of the precipitated silica. This is due to the difference in synthesis between the two silicas. While the precipitated silica exhibits spheroid-like agglomerates, the ones in fumed silica are more elongated. As a consequence, it is easier to observe pores in transmission, as in Figure 3e, for a silica that is also easier to disperse, an important functional property in many applications. Micrograph 3e shows that primary particles assemble in chains to form aggregates with a necklace shape. Therefore, the connectivity of primary particles, i.e. the number of neighbours, is lower in the case of fumed silica. Inhomogeneity exists at the particle scale, which can be seen in Figure 3e. The particle diameters range from 5 to 40 nm, with most particles between 10 and 20 nm, and some denser regions. Moreover, the primary particle shape is ellipsoidal with a longer dimension in the neighbouring direction. These effects, reported by Boldridge [42], are due to the production of fumed silica at high temperature, which causes a gradient in temperature and cooling kinetics [15,16].

Figure 3g-i are micrographs obtained from the aerogel, a dust of particles and pores down to the smallest length scale. This type of sample often results in thick objects. The global structure is highly connected and forms a network from which we tend to observe a typical pattern with a pore size of around 10 nm, in good agreement with the pore size distribution determined by Chal *et al.* [30]. Some larger pores may appear outside the agglomerates (Figure 3g-h). The similarity at different magnifications from Figure 3g to Figure 3i is representative of a fractal material. Moreover, this structure is typical of sol/gel synthesis, which promotes connectivity between primary particles rather than growth (the contrary applies regarding precipitated silica). Consequently, the primary particle is difficult to distinguish as the size of the neck joining two particles is very close to that of the particles. Such a size relationship between particle and necks was discussed by Iler [1]. Indeed, the primary length scale can be defined by a thickness that mainly ranges between 2.5 nm and 3.5 nm.

In Figure *4*, we present SANS diffractograms measured on precipitated, fumed and aerogel powders. While electron microscopy focuses on a limited area of a material, providing unambiguous details on its nanostructure, the interest of using SANS (or SAXS) resides in its representativeness since the data are averaged over a square centimetre. TEM and SANS are therefore complementary tools, enabling a deep and trustworthy analysis of the powder morphology.

The scattering intensity I = f(q) measured from precipitated silica is typical of a fractal material [69–71]. At large q values (large scattering angles), it exhibits a $l \sim q^{-4}$ dependence, indicating that the interface between the silica particles and their surrounding medium (air) is smooth. By fitting this regime with the expression $I(q) = Aq^{-4}$, one can extract the so-called Porod radius $R_p = 6\pi \Phi_{si} \Delta \rho^2 / A$ equal to 14.7 nm, which is larger than the TEM estimation (R = 7.5 nm). (In this expression Φ_{si} and $\Delta \rho^2$ are the volume fraction in silica and the scattering contrast, respectively). We believe, that this discrepancy is due to the fact that the Porod radius is calculated from the specific surface area, assuming isolated spheres, i.e. that it will increase with particles merging within an aggregate. In contrast, the TEM estimation is based on the geometrical radius of particles, regardless of the connections with their neighbours.

Thus, at intermediate q values, the inflection point position (denoted $q^* = 0.15 \text{ nm}^{-1}$ in the inset of Figure 4) is representative of the aggregate size ($R_{agg} = \pi/q^* \approx 20 \text{ nm}$), in good agreement with previous works investigating similar materials [48,70]. In addition, the non-monotonic variation of the (log-log) I(q) slope reveals the presence of an inter-aggregate structure factor [70,72] (i.e. scattering interferences), which suggests that the aggregates interact with each other. In good agreement with microscopy, the interaction distance corresponds to the diameter of the aggregates, indicating that they are in close contact.

Figure 4: SANS diffractograms measured from precipitated (blue), fumed (red) and aerogel (orange) silicas. Data are shifted vertically for clarity. The solid orange line is fitted on aerogel data with the Correlation Length model resulting in a characteristic size $\xi = 8.8$ nm and a Porod exponent m=2.1. Inset: Analog data plotted in the Kratky representation $I(q)q^2$ highlighting the q^* position in T43 and the q^{-2} dependence of the aerogel at large q.

Finally, at lower q (< 0.03 nm^{-1}), i.e. at a larger length scale, the upturn of intensity is generally assigned to network scattering. In this range the (log-log) I(q) slope is assigned to the network fractal dimension, usually slightly higher than 2 [70].

The situation is similar for the fumed powder. The main difference resides in the presence of very large particles caused by the flame synthesis (see Figure 3e above), making the particle size distribution very large. While the latter objects are not systematically observed in TEM, the SANS signal definitely contains their signature – again highlighting the synergy between the two approaches. We believe that the impact of this broad and possibly bi-disperse population in the SANS data is seen through the monotonic increase of the log-log I(q) slope with increasing q, i.e. with the disappearance of the contribution of a pronounced structure factor. In other words, this can be seen as a larger inter-aggregate distance distribution. Analogous to the precipitated sample, the Porod analysis results in $R_p = 8.4$ nm, in good agreement with our previous work providing $R_p = 7$ nm [48] and the above-mentioned TEM estimations (R=5-10 nm). Besides, the position of q^* is slightly shifted to smaller q, indicating a slightly larger average size of the aggregates (R_{agg} =30 nm) with respect to the precipitated powder.

The SANS pattern of the aerogel granules is qualitatively different. The most striking difference resides in the high-q intensity dependence, satisfying $l \sim q^{-2.1}$ (see also the plateau in the inset in Figure 4). Such a low exponent does not refer to the surface state of the particles but to the local volume fractal dimension of the material. An exponent 2 is typically encountered in polymer solutions (Θ -solvent), indicating that the objects are not dense, but rather look like hollow structures based on very thin interacting strands. Interestingly, this definition could intuitively be applied to the case of an aerogel, composed of an extremely opened structure. More quantitatively,

the typical cell size ξ of such a continuous network may be described through the Correlation length model $I(q) = \frac{I_0}{1+(q\xi)^m}$, where m is the Porod exponent and I_0 , the intensity at small q [73]. In the present case, we believe that ξ =8.8 nm must be understood as the representative cell size of the aerogel network, supporting the TEM investigation (pore size \approx 10 nm, thickness \approx 3 nm) presented above.

3.2. Improved step-by-step low-dose tomography

We present in Figure 5 electron tomography results obtained on the precipitated silica. Cross-sections from the reconstructed volume (Figure 5 a-b)) allow the observation of the interior of an agglomerate, which was way beyond resolution with TEM projections. The global architecture can be observed from the 3D models obtained by the segmentation of the reconstructed volume (Figure 5 c-d). Whatever the orientation, the 2D cross-section looks like prehistoric painting, and the 3D 500 nm-high volume like a dense cumulonimbus cloud. It first supports the structure already defined in 3.1, i.e. that of a fractal silica with agglomerates and aggregates formed by primary particles. However, it also sheds light on new elements. Although the agglomerates appeared dense in standard TEM (Figure 3a-c)), the structure is yet highly porous and open. Moreover, slightly denser regions that are barely visible with standard TEM are here easily observed. These nodes are defined by a higher connectivity, resulting in the junction of several primary particles. This scale (roughly 40-50 nm) tends to match with the aggregate size estimation made from SANS measurements (Figure 4 and [48,70]). Quantifications of porosity and pore size distribution performed by ET are shown in Figure 9 and detailed as cumulated values in SI 3. The methodology used to quantify the porosity by ET is explained in SI 4. ET is an attractive tool as it points out only the particle/aggregate scale, regardless of the inter-agglomerate scale. This gives valuable information for all composite applications using silica as a mechanical filler. This also provides data for discrete element simulation from the nanoscale.

Figure 5: Electron tomography of an agglomerate of the precipitated silica (total electron dose: 1350 e⁻. $Å^{-2}$). a-b) XY cross-sections extracted from the reconstructed volume at different depths. The silica corresponds to the darker grey level. Black dots are gold nanoparticles and the left region on image a) corresponds to the membrane supporting the sample. c-d) 500 nm-high 3D reconstruction of the previous volume with a slight angular rotation (vertical axis) between c) and d). Tens of transverse pores are revealed with very irregular shapes. The insert in the middle is a 200 nm-high 3D volume generated to highlight hanging branches of particles, one to ten particles in thickness and a tortuous open edge that could

promote the inter-penetration of objects down to the nanoscale. Movies of the reconstructed volume is available in SI2.

Regarding silica, routine nitrogen sorption measurements provide a wider range of pore analysis (at least representative from 2 to 50-60 nm for these fragile materials [74–76]). However, ET is the only technique able to capture any change in particle, neck aggregate and pore size or morphology, with a resolution equal to a few tens of nanometers. As it cannot probe multiple agglomerates and the large pores that they enclose, the porosity determined by ET (65% regarding the precipitated object in Figure 5) is always smaller than the porosity that could be retrieved from the bulk and skeletal densities (93.4 %).

Table 1: Numerical data obtained by 3D quantification performed on ET results with a resolution at least equal to 0.33nm. Branch length and junction refer to the skeleton. Two relative quantifications of junctions were computed. The first one is normalised by the solid phase volume only. The second one includes, in addition, the volume of porosity around the solid phase (as determined by ET at the agglomerate length scale). nc, not computed as refined skeleton segmentation requires new developments.

	PRECIPITATED	FUMED	AEROGEL
ET Porosity [%]	65	72	nc
Mean branch length (nm)	5.2 ± 4.4	13 ± 12	4.4 ± 3.3
Max branch length (nm)	30	130	80
Junctions by volume of solid silica phase	4.2	0.24	19
Junctions per 10 ³ nm ³ of volume of agglomerate	1.5	6.8 10 ⁻²	nc
Branches per junction	2.07	2.02	1.86

Tortuosity	1.27	1.27	1.27

Our second focus regarding quantification on a 3D model is in the solid phase. This is quite routine for X-ray tomography [77] but still a challenge for ET. In this framework, we relied on a 3D skeleton algorithm [65]. This work and the generation of the corresponding results are explained in more detail in SI6, while the numerical data regarding the three silicas are gathered in Table 1. We can therefore determine an average branch length, a distribution of branch lengths, a number of junctions in a considered volume and a tortuosity. From the portion of volume displayed in the insert of Figure 5, we obtained an average branch length of 5.2 nm. By calculating the volume of the solid phase from the 3D model, we determined 4.2 junctions in the skeleton per 10³ nm³ of silica volume.

ET results acquired on the fumed silica are presented in Figure 6. Whatever the orientation, the 2D cross-sections look like stars in a summer sky, and the 700 nm high volume like plant roots. At first glance, this confirms that fumed silica is more porous in comparison to precipitated silica. In addition, the porosity retrieved from the 3D model was 72% (96,7% as obtained from the bulk and skeletal densities), which is higher than that of the precipitated silica. Furthermore, the pore size distribution measured by ET (see SI 3) is also shifted towards higher values with respect to that of the precipitated silica. The aggregates are quite different, branched, elongated and formed by particles with lower connectivity (see the insert in Figure 6).

The quantifications performed on the 3D skeleton (see SI 5) resulted in an average branch length of 13 nm, which is significantly higher in comparison to the value obtained for the precipitated silica. There are 0.24 junction in the skeleton per 10³ nm³ of silica volume. Therefore, the skeleton retrieved from the fumed silica is less connected than that obtained on the precipitated silica.

Figure 6: Electron tomography on the fumed silica (dose: 740 e⁻. Å⁻²). a-b) XY cross-sections extracted from the reconstructed volume at different depths. c-d) 3D 500 nm high reconstruction of the previous volume with a slight angular rotation (vertical axis) between c) and d), showing the very open slender, fibrillar texture. The insert in the middle is a 3D 200nm high volume generated from a small portion of the reconstructed volume. Note the branch with various orientations formed with

particles (spotted in d)). Movies of the 3D model and skeleton are available in SI 6. The cumulative pore size distribution retrieved from ET is presented in SI 3.

Figure 7: Electron tomography of the silica aerogel (dose: 2300 e⁻. Å⁻²). a) and c) are XY cross-sections extracted from the reconstructed volume at different depths.
b) 3D 260 nm high reconstruction of a portion of the previous volume with a cut parallel to the XY plane (50 nm thick in the z direction). d) 3D reconstruction of an interior portion of volume (50 nm thick in the z direction). Movies of the 3D model

and skeleton are available in SI 7, together with a thinner 25 nm slice, revealing the net structure in graphical abstract.

ET results acquired on the aerogel are shown in Figure 6. Whatever the orientation, the 2D cross-sections look like an impressionist painting, and the 3D 260 nm high volume like a natural sponge. Working at low dose, the reconstructed volume has a low signal-to-noise ratio (see SI 7 for more details). In practice, the volume segmentation is not obvious and the volumes may include uncertainty on the thickness generated. For this reason, we did not perform quantifications on the aerogel. These must first be approached by a parametric study on several model aerogel materials, to link structures with synthesis. However, it can be seen that the structure obtained experimentally is very similar to what can be generated by molecular dynamics [78], supporting the use of this numerical tool to simulate mechanical and thermal properties.

ET highlights a very connected network and is of great value for analysing the inner texture of the aerogel. Interestingly, we observed a pattern in the porosity, with pores ranging from 5 to 15 nm and centred around 10 nm. This could be related to the semicontinuous process, with a two-step synthesis, and non-supercritical drying conditions. In the solid phase, the particle scale ranged from 2 to 4 nm. This, together with the pore size much lower than 70nm, perfectly achieves the target of obtaining superinsulation properties. Some regions within the object appear locally denser, which was not visible using standard TEM. The average branch length extracted from the skeleton (SI 5) is 4.4 nm, which is the smallest value amongst the three silicas analysed. Moreover, there are 18.8 junctions in the skeleton per 10³ nm³ of solid, which is the highest value amongst the three silicas. These characteristics, in good agreement with TEM and SANS, correspond to a highly connected network formed by small elementary blocks, with particles, branches, and pores of the same length-scale.

3.3. A tool to track ageing

Figure 8: Electron tomography results on the precipitated silica, after 96 days of ex situ ageing in a climatic chamber at 70°C and 90%RH (dose: 1000 e⁻. Å⁻²). a-b) XY cross-sections extracted from the reconstructed volume at different depths. c-d) 400 nm high 3D reconstruction of the previous volume; d) is a 120 nm thick slice of

the entire object. The porosity retrieved from ET is 48%. Movies of 3D model aged and not aged side by side are available in SI 8.

All materials will age, thus quantifying how ageing affects their nanostructures is an environmental concern: it is needed to envision the just-in-time reuse of the material in less demanding applications. We present in Figure 8 the ET results obtained on a sample of the precipitated silica aged for 96 days at 70 °C under 90% RH. The absence of artefacts in the reconstructed volume (Figure 5 a-b)) was a first hint that the object was not significantly damaged by the electron beam during the tilt series acquisition. Major differences can be seen between the unaged (Figure 5 a-b) and the aged powders (Figure 8 a-b). They are attributed to the ageing treatment, without noticeable influence of exposure to the beam. This therefore validates the pertinence of using ET as a tool for monitoring structural ageing.

Figure 9: Pore Size Distribution of the precipitated silica obtained by electron tomography, before and after hygrothermal ageing at 70 °C under 90%RH for 96 days. Direct comparison can be made as the same size increment was applied for both samples (same pixel size). Cumulative curves are available in SI3, as well as pore size distribution obtained by nitrogen sorption measurements.

The results of ET performed on the aged powder (Figure 8) highlight the fact that the primary particle size increased while ageing occurred. At this length scale, the matter appears smooth in texture with an elongation along the direction of connexion with neighbouring particles (the shape transforms from spherical to ellipsoidal). Nodes are more frequent and get thicker and larger, which reflects modifications at the aggregate scale. ET succeeds in highlighting (Figure 8) the dual origin of the fall in the overall specific surface area recorded at the global scale (from $255 \text{ m}^2.\text{g}^{-1}$ to 100 m².g⁻¹). Moreover, the pore size distribution determined via ET is shifted towards higher values after ageing (Figure 9). Structural ageing of silica occurs by displacement of matter, which modifies the material at the primary length scale and therefore redefines the porosity. These mechanisms were described in detail by Chal *et al* [30].

4. Conclusion

We highlighted the effects of electron beam on nanostructured silicas and proposed a procedure to overcome these difficulties. By combining TEM, SANS and low-dose step-by-step electron tomography, we described the structure of industrially relevant fractal silicas used as products of interest for niche applications and the mass industrial market. These powders share a multi-scale structure. From the nano to the microscale, they are composed of primary observable particles, more or less connected to each other, that form branches, nodes, aggregates, agglomerates and potentially bigger objects. At the nanoscale, pores and solid matter form an imbricated network but their specific features depend on synthesis procedures and the chemical groups grafted on the silica surface. Among the three samples quantified, the fumed silica has the lowest connectivity with primary particles that are dispersed in size (5-40 nm) and shape. Large pores can be observed between the aggregates and agglomerates. The precipitated silica has a higher connectivity and a more regular particle size, equal to 15,0±4.1 nm. Finally, the silica aerogel exhibits a network with a narrow primary scale (2-4 nm) and a regular pore pattern within 5-15 nm. Such nanoscale microstructures provide a wide range of rheological, mechanical and thermal properties. Imaging and quantifying from the nanoscale upwards opens routes towards the simulation of such properties.

Last but not least, we think that the reconstructed volumes available and the associated data quantified (size, connectivity, etc.) will be of use to implement modelling and simulation tools. Such simulations have already been performed on porous materials [44,45] but are scarce [79,80] on ultra-porous ones such as nanostructures silica with their porosities higher than 95% at the aggregate scale.

A sample of precipitated silica was aged (ex situ by setting the temperature and the relative humidity to high levels) and then analysed via low-dose step-by-step tomography, showing how it is a pertinent tool for viewing and linking textural evolution to the properties measured. ET quantifications performed on a segmented 3D model allowed the determination of the porosity and the pore size distribution of several representative objects. However, further developments are required to observe thicker samples and thus measure several agglomerates and the inter-agglomerate scale.

It would be interesting to perform in situ ageing in an Environmental TEM, to monitor the evolution of a unique 200nm high 3D object, with a resolution of several tens of nanometers. Tiny changes in necks and particles or roughness would then be qualified using ET.

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Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by ADEME, grant 1604C0019, and MATeB (joint MATEIS EDF R&D laboratory). The authors are thankful for the attribution of 4 days of experiments at LLB (CEA Saclay) and to J. Jestin for his collaboration during the measurements. We thank the Consortium Lyon Saint-Etienne de Microscopie (CLYM) for the access to the microscopes. BC, LR and GF also thank Thierry Epicier and Cyril Langlois for the in-house development of the plugin allowing the recording of electron tomography images.

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