



Facile preparation of mesoporous silica monoliths by an inverse micelle mechanism



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ABSTRACT

A well-known drawback of sol–gel materials is their tendency to crack because of the high capillary pressure supported during drying. We have pioneered a facile and low-cost route to obtain monolithic xerogels, from a silica precursor and a surfactant, mixed under ultrasonic agitation. This route presents a clear interest for practical application at industrial scale. In this paper, a model to explain the formation of silica monoliths in the presence of the surfactant is presented. It is demonstrated that a stable microemulsion of water in the silica oligomer media is produced due to the combined effect of surfactant, producing inverse micelles, and ultrasonic agitation. The model proposed, suggests that the water is encapsulated in the surfactant micelles that act as nanoreactors, producing silica primary particles. The growth of these silica seeds continues outside the micelles until the formation of the constituent particles of the xerogel. Next, the particles are packed, and mesopores are produced from the interparticle spaces. This mesoporosity prevents xerogel cracking because it reduces capillary pressure during gel drying. An in-depth investigation of the structure of the xerogels revealed that they are effectively composed of silica nanoparticles of nearly uniform size values that could match with the size of the surfactant inverse micelles. Finally, it was demonstrated that surfactant and water content present a significant effect on the final structure of the xerogels. An increase of surfactant content produces a reduction in particle size, whereas an increase of water produces an opposite effect.

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1. Introduction

In 1968, Stöber et al. [1] pioneered sol–gel route when they obtained monodisperse spherical silica particles from aqueous solutions of alkoxysilanes, with ammonia acting as a catalyst. In spite of the length of time since this synthesis, the mechanism for the formation of uniform silica particles via sol–gel reaction is still a topic of debate [2,3]. Nowadays, the formation of primary nanoparticles, acting as seeds in the first stage of the synthesis, is completely accepted [4]. However, a consensus about the particle growth mechanism has still not been achieved. Several models have been postulated to explain the particle growth, based on: addition of monomers [5,6], particle aggregation [7,8] or even a combination of these two mechanisms [9]. The monodisperse size of the silica particles was explained as a consequence of the faster growth of smaller silica particles than larger ones [9,10]. Recently, Carcouët et al. [3] proposed a growth model based on the addition

of uniform primary particles with exceptional colloidal stability and subsequent, collapse, giving rise to uniform silica particles.

An alternative route to produce monodisperse silica spheres in the nanometric range is by using inverse micelles as nanoreactors of the particles [11,12]. In this type of synthesis, water–surfactant–oil formulations giving stable microemulsions must be produced. Specifically, water should be readily solubilized in the polar core of the micelle to form water-in-oil (w/o) microemulsions, and subsequent silica formation is produced in the aqueous media located within the micelle. The droplet size of inverse micelles giving rise to the silica particle size can be modulated in the nanometer range by various parameters, in particular, the water–surfactant molar ratio [11]. In these systems, the monodispersion of the created silica particles is even greater than that associated with particles produced by the Stöber method [13].

A well-known drawback of sol–gel materials is their susceptibility to shrinkage and tendency to crack because of the high capillary pressure supported during drying [14]. Our research group has pioneered a novel sol–gel route to obtain monolithic xerogels, from silica oligomers and a non-ionic surfactant, n-octylamine, mixed under ultrasonic agitation [15,16]. We have

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chosen an oligomer (TES40) instead of the monomer (TEOS) for two reasons: (i) the sol-gel reaction is faster and (ii) the synthesis route is cheaper due to it is not a pure reagent. Both of these features are required for the real application of the products. The surfactant acts as a catalyst and as an agent that directs the pore structure of the material, giving rise to a mesoporous structure that reduces capillary pressure during drying. Silica monoliths are spontaneously produced without any additional procedures. In addition, Hydrophobic [17], water repellent [18] and self-cleaning properties [19–22] can be incorporated into these materials, by simple chemical modifications of the proposed synthesis route. The practical interest of this synthesis has been demonstrated, with some of these products being marketed under patent [23]. Moreover, several works employed our strategy (n-octylamine addition) to obtain crack-free xerogels [24–27].

An in-depth investigation of the structure of the synthesized surfactant-assisted materials was carried out in our laboratory, revealing that they are composed of practically monodisperse silica particles as a result of the role played by n-octylamine [16,28]. However, the silica particle formation mechanism was not completely understood. Recently, silica formation in a rubber matrix by the inverse micelle mechanism was proposed [2,29]. Specifically, an alkylamine (such as hexylamine or octylamine) acted as a catalyst and as nanoreactor, producing uniform silica particles dispersed in the rubber matrix. In spite of this system being different to ours because an organic phase, acting as a matrix, is involved, it is considered that a similar mechanism could be responsible for the formation of a nanoparticulated xerogel in our laboratory. In this paper, we propose a formation and growth model for the silica xerogels by an inverse micelle mechanism. Firstly, we sought evidence for the formation of inverse micelles. Secondly, we investigated the role of the surfactant as a catalyst of the sol-gel process and as a nanoreactor of the formation of silica particles by using TEM, N₂ Physisorption, FTIR and ¹H, ¹³C ²⁹Si MAS NMR measurements. Finally, a mechanism to explain formation and growth of silica particles is discussed.

2. Experimental section

2.1. Materials

TES 40 WN from Wacker (hereafter TES40), is a mixture of monomeric and oligomeric ethoxysilanes according to its technical data sheet. The average chain length is approximately 5 Si–O units. The non-ionic surfactant n-octylamine (hereafter n-8) was purchased from Sigma-Aldrich and used as received. Deodorized white spirit 15–20 (hereafter WS), which is a mixture of aliphatic and aromatic hydrocarbons, was purchased from Quimipur.

2.2. Experiments to provide evidence for the formation of a microemulsion containing inverse micelles

In order to confirm the formation of n-8 inverse micelles and a water-in-oil microemulsion, emulsions of water/n-8 in WS were prepared. As TES40 presents reactivity in water, it was replaced by WS to mimic the nonpolar nature of the TES40. Specifically, this experiment was carried out as follows: Firstly, three aqueous dispersions of n-8, with different amounts of surfactant above its solubility, corresponding to 1 M, 2 M and 3 M solutions, were prepared under magnetic agitation. Next, three emulsions were prepared by mixing WS (10 mL) and the different prepared aqueous dispersions (25 mL). The emulsions were stored for 24 h to allow migration of the micelles from the water phase to the WS phase. For comparative purposes, WS and distilled water were also mixed under the same conditions. After 24 h, all the prepared mixtures

presented two clearly differentiated (organic and aqueous) phases. The particle sizes in the obtained organic phases were measured using a dynamic light scattering (DLS) Zetasizer Nano apparatus from Malvern. Finally, 1 mL of each organic phase was added to 3 mL of TES40 in closed vials. The aim of this test was to verify the migration of water, previously encapsulated in the inverse micelle, to the WS phase. Since n-8 produces the gel transition of TES40 in the presence of water [16], the formation of a silica gel in the vial should evidence that this process took place.

2.3. Experiments to evidence the role played by the surfactant and the ultrasound to produce a microemulsion

The following experiments were carried out: (1) to test the role of n-8, 30 mL of a mixture of TES40 (29.4 mL) with n-8 aqueous dispersion (0.6 mL) was prepared under ultrasonic agitation (1 W/mL for 8 min). For comparison, another mixture was prepared according to the same protocol, but without adding n-8. (2) To test the role of ultrasonic agitation, the same mixtures were prepared, but replacing the ultrasonic agitation by vigorous magnetic stirring (600 rpm for 60 min). The formation of water/TES40 emulsions was monitored by visual inspection and their stability was checked after 24 h.

2.4. Effect of surfactant and water content on the sol-gel properties of the materials

Several silica xerogels were prepared from a starting sol containing TES40 and an n-octylamine aqueous dispersion. In order to evaluate the effect of surfactant concentration on the final texture and structure of the materials, different n-8 concentrations were employed. In addition, different water content was also employed to evaluate its effect on the material properties.

The preparation procedure was as follows: (1) Aqueous dispersions of n-8 with concentration of the surfactant significantly higher than that corresponding to its critical micellar concentration (cmc), which is 0.010 mol dm⁻³ [30], were prepared by magnetic stirring under laboratory conditions (20 °C). Turbidity of the dispersions due to the formation of micelles was clearly observed; (2) Aqueous dispersions of n-octylamine were mixed with TES40 and the mixtures were homogenized by ultrasonic agitation (1 W cm⁻³ for 8 min). Details of the n-8 dispersion volumes and concentrations employed, together with their nomenclature, are given in Table 1.

Immediately after the synthesis, the rheological properties of the sols were studied using a concentric cylinder viscometer (model DV-II+ with UL/Y adapter) from Brookfield. Experiments were performed at 25 °C maintained by the re-circulated water from a thermostatic bath. A shear stress versus shear rate flow curve was generated.

Next, the sols were cast in glass petri dishes of 3.0 cm diameter, adding 3 mL per cast. The cast sols were kept under laboratory conditions (60% RH and 20 °C). Gel transition took place spontaneously and the gel time was recorded. The stability of the sols was also evaluated by measuring the gel time in the enclosed condition. Gels were left to dry for one month. The presence of cracks in the xerogels was checked by visual inspection. Finally, all the experiments described below were carried out one month after the synthesis.

Transmission Electron Microscopy studies were carried out by using a JEOL 2010F TEM/STEM microscope, operating at 200 kV with 0.19 nm spatial resolution. Samples were prepared by depositing a small amount of the powders directly onto Lacey-Carbon coated Cu grids.

The pore volume, pore size distribution and BET surface area of the materials under study were characterized by Nitrogen Physisorption (Autosorb IQ, from Quantachrome).

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