



Synthesis of silica spheres with neutral and ionic amphiphiles and their interaction with photosensitive spiropyrans

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ABSTRACT

A study was made on the influence of ionic and non-ionic amphiphiles, i.e., CTAB and 1-(2-aminoethyl)-2-heptadecyl-2-imidazoline (**1**), on the pore hierarchy and morphology of siliceous particles synthesized with. The amphiphile (**1**) leads to formation of spherical silica particles of about 250 nm diameter, while the ionic surfactant (CTAB) led to porous silica spheres of about 750 nm diameter. A single-particle analysis using High Resolution Electron Microscopy (HREM) and Optical Density Transforms (ODT) show the inner pore structure of the particles synthesized with CTAB and low molecular weight alcohols co-surfactants (ethanol and propanol) is oriented along the sphere radius, while silica particles synthesized with (**1**) have a random-like pore structure. Both systems were used as supports for adsorption of a photosensitive spiropyran (i.e., Spiro-6) type compound (1',3',3'-trimethyl-6-nitrospiro-(2H-1-benzopyran-2,2'-indoline)) and their interaction with the silica surface was characterized by IR spectroscopy, showing a weak interaction with respect to other silicates (lamellar clays). These effects are potentially interesting for applications of biomarkers, stable photosensitive materials, solid-phase organic synthesis and dyes. The UV-vis reflectance spectra of the materials series impregnated with Spiro-6 indicated that siliceous IMP-type materials (i.e., prepared with CTAB and low molecular weight alcohols: Pr-1, Pr-2, Pr-3 and Et-1, Et-2) contained a small shoulder at 460 nm of the less conjugated protonated merocyanine form, together with a broad band at 517 nm, which corresponds to the merocyanine form. The incorporation of aluminum into the silica framework results in a single broad band at 435 nm corresponding to the protonated merocyanine form. Thus, the acidic sites created by aluminum incorporation into the silica spheres seem to favor the formation of protonated merocyanine instead of the basic merocyanine molecule.

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1. Introduction

The lyotropic properties of organic amphiphiles have been used for the synthesis of precursor mesophases in aqueous solutions, which interact with inorganic species, i.e., $\text{Si}(\text{OH})_4$, to produce a variety of mesoporous materials of technological interest [1–3]. The basic mechanism behind the formation of those mesoporous materials lays in the interaction of ionic (i.e., C_nTAB , ($8 < n < 18$), SDS) and non-ionic (i.e., L64, P123, Triton X, etc.) amphiphiles with the silica inorganic species, which are anionic entities (I^-) derived from hydrolysis of metal salts [4–10]. Thus, the inherent properties of the organic structure directing agents (SDA) and the chemical potential of the inorganic aggregates may influence the way these phases organize in solution. Among the most important interaction parameters are the molecular charge, hydrocarbon chain length and chain rigidity. In this way, mesoporous silica structures are obtained with potential properties as catalysts [11], adsorbents [12], quantum dots (matrix) [13], label biomarkers [14], column pack-

ings for high resolution chromatographic and electrokinetic separations [15], chemical sensors [16], biomarkers [17], adsorbents for hydrogen storage [18], “hosts” of chemical species [19] and catalyst supports [20] among others. In this work a newer non-ionic surfactant (1: 1-(2-aminoethyl)-2-heptadecyl-2-imidazoline) was used as SDA for synthesizing silica mesoporous materials and their structural and textural properties were compared with silica particles prepared with the CTAB surfactant. Although the synthesis conditions of both materials required slight differences with respect to the temperature and time of aging, the rest of the conditions were similar. In both cases low molecular weight alcohol co-solvents (i.e., EtOH, PrOH) were used to facilitate the primary interactions of surfactants and silica moieties at the molecular level [10]. With this purpose in mind a single-particle analysis was performed for each case using High Resolution Transmission Electron Microscopy (HRTEM) and Fourier Transform Analysis of the optical density distribution from the TEM micrographs.

Finally, the siliceous materials obtained with both surfactants types were tested as hosts of the photochromic spiropyran (1',3',3'-trimethyl-6-nitrospiro-(2H-1-benzopyran-2,2'-indoline). These compounds switch from uncolored (i.e., spirobenzopyran)

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to highly colored species (i.e., merocyanine) upon exposure to light, thus affording potential applications in optical switches and memory storage devices [21]. These spiropyran can form more stable complexes with inorganic semiconductors such as TiO₂, SnO₂, ZnO and rare earth oxides, which may lead to applications in dry color printing and sensor technologies, among others [22]. Solid-state devices based upon the spiropyran light response need a suitable support for keeping the fast response capacity of spiropyran in solution, which implies an inert support and, simultaneously, it must retain the molecule weakly for allowing it enough freedom to undergo conformational changes. In order to assess the strength of the molecular interaction between spiropyran and the surface silanol and siloxane groups of the silica hosts (i.e., those synthesized with **1** or CTAB), laminar clay (Montmorillonite) with surface acidic sites (Lewis) was compared, using IR and UV-vis spectroscopies [22]. A single-particle analysis performed by HRTEM and Computer Fourier Transform methods (CFT) was made to compare the periodicities of the inner pore structure of silica spheres that were synthesized with the new non-ionic amphiphiles (**1**) and the ionic CTAB, respectively.

2. Experimental

2.1. Chemicals

All chemicals were purchased from Aldrich and were used as received, except the stearic acid, which was purified by crystallization in absolute ethanol.

2.2. Synthesis

1-(2-Aminoethyl)-2-heptadecyl-2-imidazoline (**1**) was synthesized under microwave irradiation according to the procedure described below.

A Pyrex reaction tube with a magnetic stirring bar, containing 3.0 g of anhydrous Al₂O₃ and 20 mmol (2.08 g) of DETA (**2**) dissolved in xylene (30 mL) was heated to 70 °C. Then 2.0 mmol (0.57 g) of stearic acid was dissolved in xylene (30 mL). The resulting mixture was irradiated in a microwave oven for 15 min at 300 W. The solvent and the amine excess were distilled under vacuum and the reaction mixture was purified by flash chromatography using neutral alumina as support and hexane/benzene/dioxane/MeOH (25:25:5:5) as eluent; to yield **1** (83%) as white solid, mp 71–72 °C (Ref. [23] mp 65–66 °C); ν_{\max} (KBr) 3300, 2917, 2849, 1666, 1605 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.80 (t, *J* = 6.0 Hz, 3H, CH₃), 1.22 (s, 28H, CH₂), 1.48–1.52 (m, 2H, CH₂), 1.70–2.00 (m, 2H, CH₂), 2.02–2.15 (2H, m, CH₂), 2.70 (t, *J* = 8.0 Hz, 2H, CH₂), 2.96 (t, *J* = 8.0 Hz, 2H, CH₂), 3.02–3.15 (m, 4H, CH₂), 3.48–3.62 (m, 2H, CH₂), 5.90 (br s, 2H, NH₂); ¹³C NMR δ (50 MHz, CDCl₃) 14.0, 27.1, 27.9, 29.0, 27.9, 29.4, 29.6, 29.7, 31.8, 40.5,

50.1, 52.1, 167.4. MS (70 eV) 351 (M⁺, 50). The CMC is about 1.82×10^{-3} mol/L at 25 °C [24].

The silica based materials were prepared from tetraethoxysilane (TEOS) in aqueous solution, which was added to a solution containing the amphiphiles (i.e., **1**-type compound or CTAB) in basic media (pH = 9), as described in the following paragraphs.

The neutral compound **1** was used as structure directing agent (SDA) for the synthesis of silica mesoporous materials. As reported in Table 1 the synthesis was carried out using a 2-propanol/water (1:1) solution of **1**, adding tetraethoxysilane (TEOS) as a source of silica and ammonium hydroxide as an acidity modifier and as a catalyst for the hydrolysis of TEOS. The resulting gel was aged for 24 h at room temperature (Im-1 type materials) and at 80 °C (Im-2 type materials). After filtering the solids were treated under nitrogen atmosphere up to 550 °C and were left at this temperature in air atmosphere for 5 h. Other materials were prepared with the ionic CTAB and low molecular weight alcohols (EtOH and PrOH) as co-solvents, at room temperature, with a constant CTAB/TEOS ratio of about 4.0 (4.5 wt.% CTAB, at pH = 11.5). The CTAB/NH₄OH ratio was constant and equal to 0.076; two materials were synthesized with a CTAB/C₃H₇OH or CTAB/C₂H₅OH ratio of 0.016 (Pr-1 or Et-1), 0.010 (Pr-2 or Et-2) and 0.008 (Pr-3 or Et-3). The subsequent drying at 40 °C and calcining in air at 550 °C, for 5 h led to the materials labeled Pr-*n* or Et-*n* (where *n* = 1, 2 and 3), respectively (Table 1). These syntheses were made three times with high reproducibility. The repeatability of the synthesis of siliceous particles with CTAB and low molecular weight alcohols was also demonstrated in previous works [10,18,25].

The laminar clays (M-3) from Durango State Mines of Mexico were used as a reference for comparing the influence of surface acidity on the adsorption of organic molecules. In this respect the clays and the mesoporous materials were impregnated with Spiro-6 in acetone solution at room temperature, and then the samples were air-dried at 40 °C. After a soft grounding the powders were compressed together with about 2 wt.% KBr, to form a suitable pellet for IR transmission analysis. Also, the spectrum of the pure organic material (solid) was analyzed following the same procedure.

2.3. Characterization of physical and chemical properties

The melting point (uncorrected) of the compound **1** was determined using a Fisher Scientific apparatus. The IR spectra were recorded on a PerkinElmer 1600 spectrometer. TLC were performed in aluminum oxide 60 F₂₅₄ neutral (Type E) sheets using benzene/dioxane/ethanol (25:5:5) as eluent. ¹H (200 MHz) and ¹³C (50 MHz) NMR were recorded on a Varian Gemini-200 Instrument in CDCl₃ as solvent and TMS as internal standard. MS was obtained in electron impact (70 eV) mode on a GC-MS equipment: Hewlett-Packard 6880 (GC system) and 5973 (Mass Selective detector).

Table 1
Synthesis conditions and physico-chemical properties^a

SDA	Im-1 1 ^b	Im-2 1 ^b	Pr-1 ^c CTAB	Pr-2 ^c CTAB	Pr-3 ^c CTAB	Et-1 ^c CTAB	Et-2 ^c CTAB	Et-3 ^c CTAB
Co-solvent	C ₃ H ₇ OH	C ₃ H ₇ OH	C ₃ H ₇ OH	C ₃ H ₇ OH	C ₃ H ₇ OH	C ₂ H ₅ OH	C ₂ H ₅ OH	C ₂ H ₅ OH
t _{Aging} (h)	24	24	8	8	8	8	8	8
T _{Aging} (°C)	20	80	40	40	40	40	40	40
Mean particle diameter (nm)	250	250	750	750	750	750	750	750
Surface area (m ² /g)	187	1093	993	1100	824	939	835	876
Pore volume (cc/g)	0.12	1.3	0.86	0.91	0.73	0.82	0.84	0.76
Mean pore size (nm)	5.6	4.8	3.4	3.5	3.5	3.2	3.3	3.4

^a Reaction time = 5 h, reaction temperature = 550 °C.

^b 1-(2-Aminoethyl)-2-heptadecyl-2-imidazoline.

^c CTAB/TEOS = 4, CTAB/NH₄OH = 0.076, CTAB/Co-Solvent = 0.016.

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