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The effect of anions of transition metal salts on the structure of modified mesostructured silica films and monoliths

A. Faik Demirörs, Mehmet Arslan, Ömer Dag *

Laboratory for Advanced Functional Materials, Department of Chemistry, Bilkent University, 06800 Ankara, Turkey

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Abstract

The structure of the preformed LC mesophase of water:transition metal salt ($[M(H_2O)_6]X_2$):acid (HX):oligo(ethylene oxide) (or Pluronics):tetramethylorthosilicate (TMOS) mixture during hydrolysis and partial polymerization of the silica source is maintained upon further polymerization and condensation of the silica species in the solid state. The liquid mixture in early stage of the silica polymerization could be casted or dip coated to a surface of a glass or silicon wafer to produce mesostructured silica monoliths and films, respectively. The silica species and ions (metal ions and anions) influence the structure of the LC mesophases (as a result, the structure of silica) and the hydrophilic and hydrophobic balance in the reaction media. The silica structure can be changed from hexagonal to cubic by increasing, for example, the nitrate salt concentration in the nitrate salt systems. A similar transformation takes place in the presence of very low perchlorate salt concentration. The salt concentration in the mesostructured silica can be increased up to 1.1/1.0 salt/SiO_2 w/w ratio, in mesostructured silica materials by maintaining its lamella structure in P123 and cubic in the C_nEO_m systems. However, the materials obtained from the P123 systems undergo transformation from lamella to 2D hexagonal upon calcinations. The method developed in this work can be used to modify the internal surface of the pores with various transition metal ions and metal oxides that may find application in catalysis.

Keywords: Mesostructured; Liquid crystals; Transition metal ions; Non-ionic surfactants; Pluronics

1. Introduction

Since the first reports [1,2] on the synthesis of mesoporous molecular sieves (designated as M41S) that have well-defined channels and uniform pore sizes, there have been extensive efforts towards the synthesis of new functional materials [3–5] and towards the understanding of the formation mechanism of mesoporous silica materials [6–8]. A liquid crystal templating (LCT) mechanism for the M41S family, particularly MCM-41, was proposed due to the similarity between the liquid crystalline surfactant assemblies and M41S family [6]. Later a generalized liquid crystalline templating mechanism [7,8] was suggested based on the electrostatic interaction of inorganic species and the head groups of the surfactant molecules. The lyotropic liquid crystalline mesophase of an oligo(ethylene oxide) surfactant was first used by Attard et al. for the synthesis mesoporous silica monoliths [9]. In this assembly process, the silica source, tetramethylorthosilicate (TMOS) was directly added into the previously existing LC mesophase to produce mesostructured silica. In this method, the existence of the LC mesophase is more important than the interaction of the silica precursors and the surfactant cooperation to form the mesophase.

Stucky et al. introduced a family of highly ordered mesoporous silica using oligo(ethylene oxide) type non-ionic surfactants ($C_nH_{2n+1}(OCH_2CH_2)_mOH$, denoted as C_nEO_m) and triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) copolymers, pluronics in an acidic media [10]. They found that the non-ionic

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* Corresponding author. Tel.: +90 312 290 3918; fax: +90 312 266 4579.
E-mail address: dag@fen.bilkent.edu.tr (Ö. Dag).

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surfactants frequently form cubic or 3D hexagonal mesoporous silica structures, whereas the non-ionic triblock copolymers tend to form 2D hexagonal (*p*6*mm*) mesoporous silica structures. In the pluronic system, the EO/PO ratio of the copolymers is an important parameter; decreasing this ratio of the triblock copolymer leads to the formation of lamella mesostructured silica, while increasing it promotes cubic mesostructured silica formation [10]. Göltner and co-workers [11] showed that non-ionic amphiphilic diblock copolymers with a polyethylene oxide head group and a polystyrene tail group could also be used as a template to create crack-free mesoporous silica monoliths. Note also that the C_nEO_m type surfactants have been successfully applied to prepare mesoporous transition metal oxides that are not accessible using the electrostatic templating method [12–14]. The metal alkoxides that readily hydrolyze to the corresponding metal oxide can also be templated using C_nEO_m type non-ionic surfactants [12,13].

A new lyotropic liquid crystalline (LLC) mesophase that only contains C_nEO_m surfactant and transition metal salts (TMS) (without water) [15] has recently been introduced by our group. In this binary system, the transition metal aqua complexes induce the C_nEO_m surfactants to self-assemble into an LC mesophase, which is stable for years [15]. The structure of the $[M(H_2O)_x](NO_3)_2$:C_nEO_m binary mesophases usually display a 2D hexagonal mesostructure in nitrate salt systems and a cubic mesostructure in the $[M(H_2O)_x](ClO_4)_2$:C_nEO_m systems [16]. However, the binary chloride salt systems do not have the mesophase. Indeed the chloride TMSs are almost insoluble in the oligo(ethylene oxide) surfactant media [16].

Usually an electrolyte is added to improve the structural properties of the materials [17]. The addition of electrolytes is also known to affect the structure of the LC mesophases [18–22]. This effect has been known for more than a hundred years as the Hofmeister effect [23]. Anions such as SO_4^{2-} and Cl^- that decrease the solubility of the surfactants are known as "salting-out" anions, water structure-makers or cosmotropic ions and the others such as NO_3^- and ClO_4^- that increase the solubility of the surfactants are known as "salting-in" anions, water-structure-breakers, or chaotropic anions [24]. Note that the electrolytes are almost always present in the synthesis of mesoporous materials. Salts are known to have a significant effect on the formation mechanism of mesoporous materials. Electrolytes generally increase the stability of the materials by improving the interface properties. Ryoo and Jun [25] have improved the stability of mesoporous silica by using various salts. Stucky et al. [26] found that the addition of extra salt stimulates the formation of single crystal materials instead of amorphous materials.

In this work we have studied the effect of salt type and amount on the synthesis of mesostructured silica films and monoliths, produced by LCT approach using C_nEO_m and Pluronics and transition metal salts. The resulting materials were characterized using diffraction (XRD), microscopy (POM and TEM), and spectroscopy (FT-IR and micro-Raman) techniques.

2. Experimental

All chemicals and solvents were reagent grade and used as received without any further treatment. The triblock copolymers, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO–PO–EO), P65 ($PEO_{20}PPO_{30}PEO_{20}$, $M_{av} = 3500$) and P123 ($PEO_{20}PPO_{70}PEO_{20}$, $M_{av} = 5800$) were generously donated by BASF Corp. and used without further treatment. Cobalt(II)nitrate hexahydrate($[Co(H_2O)_6](NO_3)_2$), 98% pure), cobalt(II)chloride hexahydrate ($[Co(H_2O)_6]Cl_2$, 98% pure), cobalt(II)perchlorate hexahydrate ($[Co(H_2O)_6](ClO_4)_2$), zinc(II)nitrate hexahydrate ($[Zn(H_2O)_6](NO_3)_2$)and zinc(II)perchlorate hexahydrate ($[Zn(H_2O)_6](ClO_4)_2$) were obtained from Aldrich, Germany. HNO_3 and $HClO_4$ were obtained from Aldrich, Germany. Tetramethylorthosilicate (TMOS, %98 pure) was obtained from Aldrich and Fluka.

2.1. Preparation of liquid crystalline mesophases with transition metal salts

The surfactant:water:metal salt samples were prepared either by mixing 1.0 g of $C_{12}EO_{10}$ with 1.0 g of water and then adding the transition metal salt (TMS) complexes to the mixture, or the TMS was first dissolved in water and then the surfactant was added to the mixture. The mixture was homogenized by a few heating (to the melting point) and cooling (to room temperature (RT)) cycles. The TMS/surfactant mole ratios was varied from 0.0 to 15.0. These samples were either examined in their LC mesophases or used further in the synthesis of mesostructured silica.

2.2. Synthesis of mesoporous silica by liquid crystalline templating (LCT)

A mixture containing 1.0 g deionized water, *x* g TMS (*x* was varied between TMS/$C_{12}EO_{10}$ mole ratio of 0.0 and 4.0), HX (0.1 g) (acid, $X = NO_3^-, ClO_4^-$ or Cl^-) and 1.0 g $C_{12}EO_{10}$ was prepared by first dissolving TMS in deionized water containing HX. Upon addition of $C_{12}EO_{10}$, the mixture was homogenized by heating at around 60 °C for a few minutes to get a clear solution (note also that the mixture is a paste at low salt concentrations and a solution at higher salt concentrations). To the clear mixture, 1.7 g tetramethylorthosilicate (TMOS) was added at once. The mixture became a clear solution upon shaking the mixture for a few minutes or gentle heating over a hot plate. The nitric acid (HNO_3), perchloric acid ($HClO_4$) and hydrochloric acid (HCl) have been used as acid sources to speed up the silica polymerizations in the metal nitrate, metal perchlorate and metal chloride systems, respectively.

Water (3.0 g), *x* g TMS (*x* corresponds to TMS/P123 mole ratios of 0.0–9.0), 0.1 g HX (acid, $X = NO_3^-, ClO_4^-$ or Cl^-) and 1.0 g P123 or P65 were mixed in the same order as in $C_{12}EO_{10}$ case. Then, the mixture was homogenized by stirring with a magnetic stirrer for 15 min, and then 1.7 g of TMOS was added as the silica source. The clear solutions