



Fluorocarbon and hydrocarbon functional group incorporation into nanoporous silica employing fluorinated and hydrocarbon surfactants as templates

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ABSTRACT

Ordered mesoporous hydrocarbon functionalized (*n*-decyl) silica samples are synthesized by the 'one-pot' (direct) synthesis method using two cationic fluorinated surfactants, C₆F₁₃C₂H₂NC₅H₅Cl (HFOPC) and C₈F₁₇C₂H₂NC₅H₅Cl (HFDePC), and a typical hydrocarbon surfactant, C₁₆H₃₃N(CH₃)₃Br (CTAB), as templates. The properties of the materials are compared to those of silica samples functionalized with a fluorocarbon functional group, heptadecafluoro-1,1,2,2-tetrahydro-decyl, whose fluorocarbon separating ability was reported earlier [33]. The pore characteristics, organic loading, and wetting properties of the resulting materials are determined for the following combinations of surfactant/functional groups: hydrocarbon/hydrocarbon, hydrocarbon/fluorocarbon, fluorocarbon/hydrocarbon and fluorocarbon/fluorocarbon. Synthesis using the longer chain fluoro-surfactant (HFDePC) template results in the highest incorporation of both *n*-decyl and fluorocarbon functional groups, with a corresponding loss of long-range pore order in the fluorinated material. Materials synthesized using the HFOPC template have very low levels of functional group incorporation compared to the HFDePC-templated materials. CTAB-templated materials display greater long-range pore order than the fluorocarbon templated materials. The incorporation of the fluorocarbon functional precursor is more effective (on a % yield basis) than the hydrocarbon functional precursor for silica materials synthesized using CTAB. Similarly, the use of fluorinated surfactant templates enhances fluorocarbon incorporation relative to hydrocarbon incorporation in the mesoporous material. Solubility of the precursors (*n*-decyltriethoxysilane and heptadecafluoro-1,1,2,2-tetrahydro-decyltriethoxysilane) in the synthesis medium and favorable aggregation behavior of the alkane/fluoroalkane functional groups with the surfactant micelles improves the incorporation of the functional group.

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1. Introduction

Synthesis of organically functionalized nanoporous silica is an active research area because of the broad range of potential applications of these high surface area materials in sensing, catalysis and separation. Surfactant templating of sol-gel derived silica results in large surface areas, large pore volumes and narrow pore size distributions. Also, the pore size and structure can be tailored for specific applications by using surfactants with different hydrophobic tails and varying the synthesis conditions. Since the discovery of the M41S family of nanostructured materials [1], various organic functional groups have been incorporated into mesoporous silica by means of post-synthesis grafting or direct co-condensation of organofunctional silanes and silica precursors [2].

Synthesis of functionalized mesoporous silica by co-condensation results in high degrees of functional group incorporation [3]. Lim and Stein [3] and Kruk et al. [4] investigated vinyl incorporation by co-condensation in the presence of cetyltrimethylammonium bromide (CTAB) as a pore template. An increase in vinyl content decreases the pore size (moving from mesoporous to microporous materials), pore volume and order of the materials. This is consistent with our observations of reduced long-range order, pore size, surface area and pore volume with increasing vinyl content when partially fluorinated surfactants were used as templates to synthesize vinyl functionalized nanoporous silica [5]. Primary amines and secondary amines have also been incorporated into mesoporous silica by employing cationic surfactants (e.g. CTAB) [6], anionic surfactant (sodium dodecylsulfate, SDS) [7], nonionic surfactants [8] and block co-polymers [9] as templates. In addition, other functional groups, such as thiol groups (mainly mercaptopropyl functionalization) [10–14] and, more recently,

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organic bridging groups [15,16] have been incorporated into mesoporous silica through co-condensation of their corresponding silica precursors with tetraalkoxysilanes. Bi-functionalized nanoporous silica materials (e.g., ureidopropyl with 3-[2-(2-aminoethylamino)ethylamino]-propyl [17], sulfonic acid-amino groups [18] and carboxyl-amino groups [19] functionalized silica) have also been prepared by co-condensation synthesis. Post-synthesis attachment to reactive organic sites in these organic/inorganic composites has been used to further functionalize mesoporous silica, for example, with biomolecules [20–22].

Numerous investigations have examined hydrocarbon-based templates [2,23–25] and, more recently, fluorocarbon surfactant templates [26–31] for the synthesis of mesoporous silica. However, organic functionalization has focused primarily on the incorporation of hydrocarbon, not fluorocarbon, functional groups. There are limited examples of fluorocarbon incorporation into mesoporous silica [32–37]. Fluorocarbon functionalization of silica results in a surface with increased hydrophobicity and lipophobicity [36]. The applications of fluorinated surfaces, which are “solvent responsive” include their use in chromatographic purification and separation of fluorinated compounds [33,38–40], in fluorous biphasic catalysis [40,41] and as hydrophobic surface coatings [36,42]. Low-surface tension mobile phases such as fluorocarbon solvents and supercritical carbon dioxide effectively wet the surfaces of fluorocarbon-functionalized silica, allowing for their effective use for separation processes. Fluorocarbon-incorporated porous silica can also be used as a low- k dielectric for semiconductor devices [35].

The hydrocarbon–hydrocarbon interaction of traditional surfactant templates and organic functional groups, as well as the hydrophobic or hydrophilic nature of the functional group, determine the orientation of the functional group within the pores during direct synthesis of organic functionalized mesoporous silica [43–45]. The interaction of organic functional groups with the surfactant can be compared to alcohol interaction with cationic surfactants. For example, the role of alcohol in the formation of C_n TAB (alkyltrimethylammonium bromide) aggregates changes from co-solvent to co-aggregate to co-surfactant with increasing alcohol chain length [46]. Matching the chain length and chemical nature of a hydrophobic group and the surfactant hydrophobic tail promotes the incorporation of the hydrophobic group in surfactant micelles, improving solubilization and stability of the aggregate [47].

Post-synthesis attachment has been the primary method to prepare fluorocarbon-functionalized silica [48]. When extending direct synthesis approaches to fluorocarbon-functionalized material, the nature of the surfactant/organic precursor interactions (e.g., hydrocarbon surfactant template/fluorinated silica precursor) is expected to influence the self assembly process. Mixtures of hydrocarbon and fluorocarbon surfactants may form uniformly mixed aggregates or segregated hydrocarbon rich and fluorocarbon rich micelles or mixed micelles with de-mixed hydrocarbon and fluorocarbon regions [49,50]. Aggregation behavior of hydrocarbon and fluorocarbon surfactant mixtures is a function of the surfactant chain lengths, hydrophobic chain structure (e.g. aromaticity and branching), concentration, and temperature [51,52].

The role of perfluoroalkyl chain length in surfactant assembly and its effect on the silica mesostructure was investigated in the synthesis of fluorinated organosilicate films by solvent evaporation using CTAC as template [35]. The fluorocarbon-functionalized silica films display both hexagonal and cubic mesostructure for short chain functional group (Rf_h) and only hexagonal structure for the long chain functional groups (Rf_{6h} and Rf_{8h}). An increase in the hexagonal cell parameter and pore wall thickness with increasing perfluoroalkyl chain length is attributed to the extension of fluorocarbon groups in the pore channel [35]. Porcherie et al. [37] have also examined templating with hydrocarbon and fluo-

rocarbon surfactants in the synthesis of fluorocarbon-functionalized silica, thus providing the first investigation of the effect of fluorocarbon surfactant/fluorocarbon functional group combination on silica materials properties. The use of cationic fluorinated surfactant template resulted in disordered porous silica with low fluorocarbon incorporation for a long chain fluorinated functional group (Rf_h), even at a high TEOS to functional precursor ratio of 19:1. Improved fluorocarbon incorporation and material order were observed when a short chain fluorocarbon ($CF_3(CH_2)_2$ - or Rf_h) functionalized silica was synthesized, suggesting that incorporation of the long chain functional group disrupts the self assembly of the cationic fluorinated surfactant micelles. In a study of the preparation of fluoroalkane-functional materials for fluorophilic separations, we found contrary evidence that pore order could be retained even with a large amount of fluorocarbon-based silane [33]. However, the degree of incorporation of the functional group and the effects of the nature of the functional group (hydrocarbon vs. fluorocarbon) required more systematic investigation to understand how they influence materials physical properties.

This work examines the effect of combinations of hydrocarbon and fluorocarbon templates and functionalized silica precursors on the material textural properties, pore structure, long-range order and functional group loading of functionalized silica formed by direct synthesis. The incorporation of fluorocarbon functional group (heptadecafluoro-1,1,2,2-tetrahydro-decyl; perfluoro-decyl) and its hydrocarbon analogue (n -decyl) is investigated using CTAB (cetyltrimethylammonium bromide), HFOPC (tridecafluoro-1,1,2,2-tetrahydro-octylpyridinium chloride) and HFDePC (heptadecafluoro-1,1,2,2-tetrahydro-decylpyridinium chloride) as templates. We demonstrate the incorporation of a longer chain fluorinated group with a much higher ratio of the functionalized precursor to tetraethoxysilane than has been examined previously [37]. The influence of hydrocarbon/fluorocarbon surfactant/template interactions on functional group incorporation, mesostructure and physical properties of the silica is examined.

2. Materials and methods

Tetraethoxysilane (TEOS; Fig. 1) with a purity of 99% was obtained from Fluka Chemika. n -Decyltriethoxysilane ($H_{10}TES$, 95% purity; Fig. 1) and heptadecafluoro-1,1,2,2-tetrahydro-decyltriethoxysilane (Rf_hTES , 95% purity; Fig. 1) were purchased from Gelest Inc. CTAB (99% purity; Fig. 2) was obtained from Sigma. The fluorinated surfactants (Fig. 2), $C_{6}F_{13}C_2H_4NC_5H_5Cl$ and $C_8F_{17}C_2H_4NC_5H_5Cl$, labeled HFOPC and HFDePC, respectively, were synthesized as previously described [5].

2.1. Synthesis of mesoporous silica

Functionalized mesoporous silica was synthesized by utilizing a 4:1 mole ratio of TEOS to Rf_hTES or $H_{10}TES$. Particles were prepared from aqueous solutions for CTAB and HFOPC-templated materials. HFDePC-templated materials were prepared from homogeneous water/ethanol solution, where the addition of ethanol was required to obtain ordered structures. Non-functionalized materials were synthesized as previously described [5].

Materials synthesis began by adding the surfactant to de-ionized ultra-filtered water (DIUFW) and ethanol (if used), and stirring the mixture for 5 min. Concentrated ammonia (catalyst, 28–30% solution from Malinkrodt) was then added with continuous stirring of the mixture for an additional 10 min, after which TEOS or a mixture of TEOS and Rf_hTES (or $H_{10}TES$), in the desired proportions, was slowly added. The mixture was aged with stirring at room temperature for 24 h. The molar ratios of the reactants used in the syntheses were 186 DIUFW:0.184 CTAB (or 0.082

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