

Amphoteric surfactant templating route for mesoporous zirconia

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An amphoteric surfactant templating route permits the synthesis of hexagonal mesophases of zirconium compounds by self-assembly of the surfactant and soluble zirconium species in aqueous solution.

The invention of mesoporous silica molecular sieves^{1,2} has generated wide interest in the synthesis of mesoporous materials based on self-assembly of ordered, surfactant/inorganic structures. Routes based on ionic,¹⁻⁴ hydrogen,^{5,6} and covalent bonding⁷⁻⁹ between the surfactant and the inorganic have been developed for the synthesis of mesoporous silica and other metal oxides. Previously, mesoporous zirconia has been produced; however, these methods involve expensive alkoxides,¹⁰ rely on sulfate ion to link the surfactant and zirconium,^{11,12} or do not involve self-assembly.^{13,14} Here, we report a new synthesis route based on self-assembly of a soluble zirconia precursor and an amphoteric surfactant template. The amphoteric surfactant, cocamidopropyl betaine (CAPB), has quaternary ammonium and carboxylate functionalities for the head group and can therefore bond with both negatively and positively charged inorganic species. In contrast to quaternary ammonium surfactant routes,^{11,12} CAPB does not require a bridging anion for the formation of the surfactant-Zr complex. CAPB also has the advantage of high solubility over wide ranges of pH and ionic strength¹⁵ and may therefore find use in a variety of syntheses.

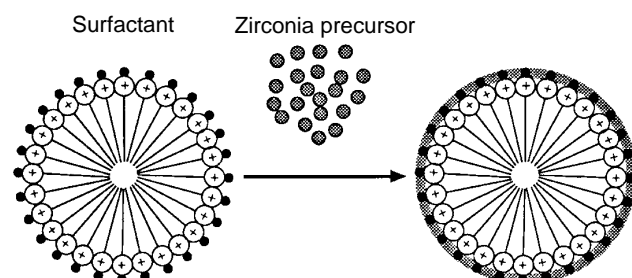
The proposed amphoteric surfactant templating route is shown in Scheme 1. Under the low pH conditions of the reaction, the quaternary ammonium group of CAPB is positively charged, and the carboxylate group is initially protonated.¹⁶ Positively charged inorganic species attach to the surfactant by reaction with the carboxyl group. Concurrent surfactant bonding with the inorganic and aggregation of the micellar structures leads to formation of the hexagonal mesophase. The quaternary ammonium group serves two purposes: (i) it imparts high solubility for the otherwise insoluble carboxylic acid and (ii) it helps to ensure a large head-group area necessary for the formation of the rod-shaped micellar subunits of the hexagonal phase.¹⁷

The hexagonal mesophase was prepared from zirconyl chloride octahydrate (Aldrich Chemical), cocamidopropyl betaine (Amphosol CG, 30 mass%, Stepan Co.) and water, as

follows. CAPB was purified of NaCl by ion exchange to pH = 2.6. Aqueous 0.25 M ZrOCl₂ was combined with CAPB until the Zr/CAPB mole ratio was 0.8. After reaction at 70 °C for four days the product was recovered by filtration.

Powder X-ray diffraction (XRD, Cu-K α radiation) of the as-synthesized mesophase (Fig. 1) revealed a primary (100) reflection corresponding to 41 Å and a secondary (110) reflection of the hexagonal phase. Higher order peaks of the hexagonal mesophase were unresolved, in part because of a broad peak centred at 2θ ca. 5.2°. This broad peak suggests that the walls of the mesostructure are made up of amorphous zirconium hydrate, since the peak approximately corresponds to a *d*-spacing of 17 Å, the average distance between zirconium centres in crystalline hydrates.¹⁸ Other evidence for tetrameric species is given by three more broad peaks centred at 2θ ca. 27, 42 and 58° (XRD not shown) which correspond to zirconium tetramers in solution.¹⁹ Transmission electron microscopy (TEM) of as-synthesized mesophase (Fig. 2) confirmed the formation of the hexagonally packed mesostructure. The 42 Å repeat distance from TEM agrees well with d_{100} = 41 Å from XRD.

Bonding between the surfactant and zirconium precursor was probed by solution ¹³C NMR spectroscopy. Betaine [(carboxymethyl)trimethylammonium hydroxide, Aldrich Chemical] was used to model the interactions of the surfactant head-group with zirconium species during the early stages of mesophase formation. The use of betaine in place of CAPB prevented precipitation, allowing the collection of simplified high-resolution solution NMR spectra (Fig. 3). Chemical shifts were referenced to dioxane (δ 67.4). Betaine on its own [pH adjusted to 1.3 with HCl, Fig. 3(a)] showed three distinct peaks: one at δ 54.00 corresponding to the methyl carbons, one at δ 63.63 corresponding to the methylene carbon and one at δ 167.03 corresponding to the carbon of the carboxyl group. Addition of zirconyl chloride [Zr/betaine molar ratio = 1, pH = 1.3, Fig. 3(b)] caused peak shifts for the carboxyl carbon (δ 2.04) and methylene carbon (δ 1.45). A previous study has shown that the carboxyl carbon peak shifts to lower field upon deprotonation (increasing pH).²⁰ Since the pH values were the same for the zirconium-betaine and betaine solutions, the significant peak shift is mainly caused by the interaction of the carboxylate



Scheme 1 Proposed amphoteric surfactant templating route for hexagonal mesophase formation where the carboxylate group provides for the bonding of the surfactant with the inorganic species and the quaternary ammonium group maintains a large head-group area for hexagonal mesophase formation

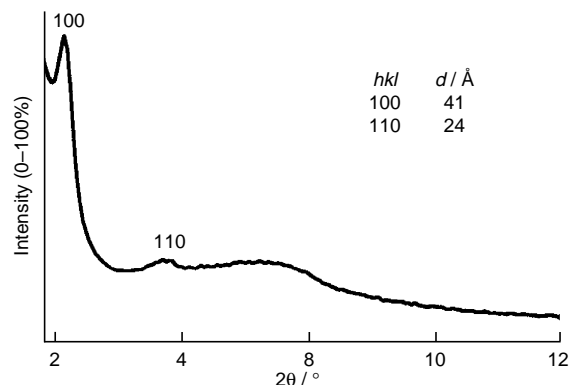


Fig. 1 Powder X-ray diffraction pattern of the zirconyl chloride hexagonal mesophase showing the 100 and 110 reflections of a hexagonal lattice

group with the zirconium species. Furthermore, bonding between the carboxylate group and zirconium species is supported by a decrease in mobility, as indicated by the broadening of the carboxylate and methylene peaks. Multiple carboxylate peaks suggest a variety of bonding conformations in the betaine–zirconium complex. Peak shifting and broadening of the methyl carbon peak by zirconyl chloride were insignificant, indicating that the quaternary ammonium group does not bond with the zirconium species.

As-synthesized hexagonal mesophases prepared by the amphoteric surfactant templating route showed poor thermal stability. Calcination caused the (100) reflection of the hexagonal mesophase prepared from zirconium sulfate to shift to higher angle, indicating shrinkage of the mesostructure. Concurrently, higher order reflections of the hexagonal meso-

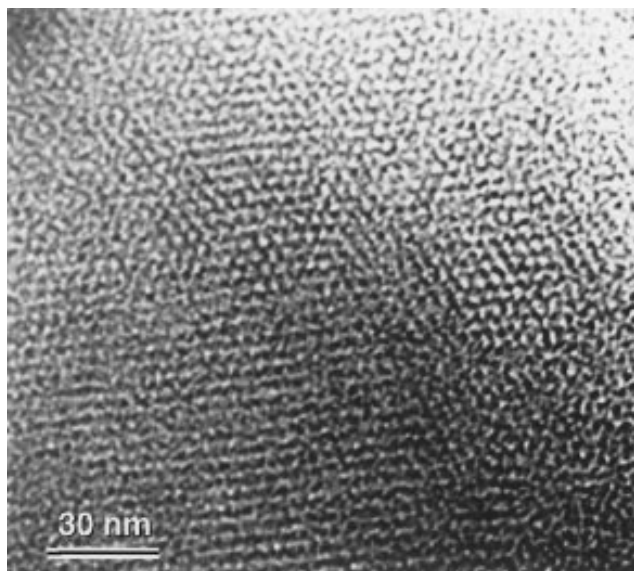


Fig. 2 Transmission electron micrograph of the zirconyl chloride hexagonal mesophase produced by the amphoteric surfactant templating route showing the 42 Å repeat distance

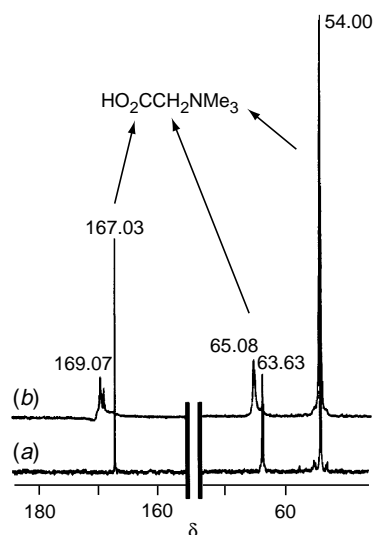


Fig 3 Solution ^{13}C NMR spectra of betaine, pH adjusted to 1.3 (a) and of the betaine–zirconyl chloride complex; (b) Zr–betaine mole ratio = 1, pH = 1.3

phase disappeared. Such loss of long-range order occurred as structural water, counter ions, and surfactant were removed simultaneously during calcination. These problems might be solved by innovative methods for removing the surfactant template and condensing the oxide precursors.^{8,9} For example, controlled base treatment with NaOH proved to be efficient at removing the counter ions without destroying the mesostructure. Base-treated zirconium sulfate mesophase had surface areas of $130\text{ m}^2\text{ g}^{-1}$ after calcination at $350\text{ }^\circ\text{C}$ and $40\text{ m}^2\text{ g}^{-1}$ after calcination at $450\text{ }^\circ\text{C}$, as compared to $<5\text{ m}^2\text{ g}^{-1}$ for calcined, as-synthesized material.

In summary, an amphoteric surfactant templating method has been developed for the self-assembly of hexagonal mesophase zirconium compounds. Cocamidopropyl betaine provides the appropriate head-group area, solubility and chemical bonding to produce a hexagonal mesophase from aqueous solution. The quaternary ammonium group ensures large head-group area and high solubility, while the carboxylate group chemically attaches the precursor to the surfactant. Bifunctional surfactants, such as CAPB, offer new possibilities in mesoporous syntheses, particularly those involving cationic inorganic species.

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