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Mixed surfactants-directed the mesoporous silica materials with various morphologies and structures

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ABSTRACT

A new mixed surfactants system using alkyl carboxylic acids and quaternized poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl] urea] (PEPU) as the co-template was used to synthesize mesoporous silica materials with various morphologies and structures, including flakes, regular spheres, nanoparticles, and tube-spheres. The cationic polymer connected the anionic surfactant micelle to the anionic polysilicate species to induce the synthesis of the mesoporous silica materials. The structure and property of the surfactant and the cationic polymer determined the formation of mesoporous silica, and also had a signification influence on the morphology and structure of the final materials. To further explore the possible formation mechanism of these mesoporous materials, zeta potential was utilized to evaluate the interaction between the anionic surfactant and the cationic co-template. In addition, the structure, morphology, and porosity of these materials were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption–desorption measurements.

1. Introduction

Large surface area and pore volume, tunable pore sizes, and splendid morphologies and structures make the ordered mesoporous silica materials ideal for the application of bio-separation, adsorption, catalysis, and drug delivery [1–5]. Recently, many groups have been interested in using various surfactants to synthesize novel mesoporous materials for their special potential applications. The use of cationic surfactants [6], anionic surfactants [7–9], nonionic surfactants [10], neutral amine surfactants [11], block copolymer surfactants [12,13], and even the mixed surfactant systems have been reported in recent years. In the mixed surfactant systems, hydrophobic stuffing-surfactant [14,15], cosolute-surfactant [16], cationic–anionic surfactants [17–23], cationic–nonionic surfactants [24–26], and anionic–nonionic surfactants [27,28] have been studied. The assembly mechanism of the mixed surfactants system can be divided into two aspects: one is the solubilization of a hydrophobic agent, like 1,3,5-triethylbenzene (TMB) and 1,3,5-triisopropylbenzene (TIPB), inside the hydrophobic portion of the ordered surfactant mesophases. The other is the solubilization of a cosolute, such as alcohol and amphiphilic surfactant, in the palisade layer of the micelle formed by the surfactant. Both cases change the packing parameter g significantly ($g=V/al$, where V is the effective volume of the surfactant tail region, a is the effective head-group area at the micelle surface, and l is the surfactant tail length), which makes the mixed surfactants system always induce the special morphologies and structures.

TIPB was used as a filling agent to increase the pore size of SBA-15 with the pore diameter varying from 10 to 26 nm, even further to 50 nm with heterogeneous structure [15]. Ryoo et al. used cationic alkyltrimethylammonium bromides and poly (ethylene oxide) alkyl ethers surfactant mixtures as structure directing agents to prepare MCM-48 with high yield [24]. And the surfactant mixture of triblock copolymer P123 and *n*-butanol was also used to synthesize cubic $Ia\overline{3}\,d$ mesostructure with pore size ranging from 4 to 12 nm. The cubic phase domain is remarkably extended by controlling the amounts of butanol and silica source correspondingly [16]. Hollow spheres [23] and ellipsoidal nano-podlike mesoporous materials [22] were also templated from the alkyl trimethylammonium bromide (CTAB)/fluorocarbon surfactant systems. A mixture of CTAB and decanoic acid has been used as the structure directing agents in the synthesis of vesicle-like patterned mesoscopically ordered silica in the presence of toluene [21]. He et al. reported the synthesis of mesoporous silica nanomaterials with varied morphologies and pore structures, including nanospheres, nanoellipsoids, helical nanorods, and multi-lamellar nanovesicles using cetyltrimethylammonium bromide and sodium bis (2-ethylhexyl) sulfosuccinate as co-template [29].

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Generally, in basic condition, the anionic surfactant cannot induce the synthesis of the mesoporous silica materials due to the unmatched interaction. The use of silane coupling agent to connect anionic surfactant to anionic silica species make anionic surfactant inducing the mesoporous silica materials come true [8,9]. In this paper, we try to introduce a cationic polymer, poly[bis(2-chloroethyl) ether-alt-1,3-bis[3- (dimethylamino)propyl]urea] (PEPU), as the new co-template to assist the anionic surfactant to induce the synthesis of the mesoporous silica materials. And, alkyl carboxylic acids with different chain lengths, including lauric acid, myristic acid, palmitic acid, and stearic acid were used as the anionic surfactants. The final meosporous materials with various morphologies and structures, such as flakes, regular spheres, nanoparticles, and tube-spheres were synthesized using the new mixed surfactants system.

2. Experimental

All chemicals were used as received without further purification. Poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea], quaternized (62 wt% in H_2O), poly(diallyldimethylammonium chloride) (35 wt% in H_2O) and dodecyltrimethylammonium bromide (C12TAB) were purchased from Aldrich. Lauric acid, myristic acid, palmitic acid, and stearic acid were obtained from Tianjin Chemical Company. Tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH), and cetyltrimethyammonium bromide (C16TAB) were purchased from Beijing Chemical Company. Deionized water was used in all experiments.

Mixed surfactants system: in a typical synthesis, lauric acid (0.5 mmol) was dissolved in a solution containing H_2O (20 mL), ethanol (1 mL) and NaOH solution (3.1 mL, 0.2 M) at room temperature. PEPU aqueous solution (0.27 g, 10 wt %) was added and the mixture was stirred for 2 h. Then, 3 mL of TEOS was added and the mixture was continuously stirred for another 24 h. The solid samples were collected by centrifugation, washed with ethanol three times and dried at 60 °C. The template was completely removed by extraction in an ethanol–HCl mixture for 10 h, followed by calcination at 550 °C for 5 h in air condition. The synthetic details of other surfactant/polymer systems are summarized in Table 1.

The synthesis of MCM-41_{16}/MCM-41_{12} using C16TAB/C12TAB as the template has already been described in previous report [30]. In a typical procedure, a system with 3.00 g of C16TAB (2.54 g of C12TAB), 0.35 g of NaOH and 30 mL of H_2O was heated and stirred until a clear solution was obtained. Then 3 mL of TEOS was added and the system was continuously stirred for another 24 h at 60 °C (at room temperature for C12TAB system). The final sample was collected by filtration and washed with plenty of water. After dried at 60 °C overnight, the material was calcined to remove the template at 550 °C for 5 h.

Small-angle XRD diffraction (SAXRD) data were collected on a SIEMENS D5005 diffractometer with Cu $K\alpha$ radiation at 40 kV and 30 mA. Particle morphologies of these materials were determined by a scanning electron microscope (SEM) using JEOL-JSM-6700F operating at an accelerating voltage of 5 kV, and transmission electron microscope (TEM) images were recorded on JEOL 3010 with an acceleration voltage of 300 kV. Nitrogen adsorption–desorption was measured using a Micromeritics ASAP 2010 M adsorptometer. Before measured, the samples were degassed at 423 K for 12 h, and the measurement was carried out at 77 K. Specific surface areas and pore size distributions were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models from the adsorption branches, respectively. The zeta potential of the precursor solution was evaluated by BROOKHAVEN ZetaPALS. FT-IR spectrometer (JASCOFT/IR-420) was used to record infrared spectra of the samples by the KBr method. Powder materials were pressed into a tungsten mesh grid and installed in an situ FT-IR transmission cell, and the samples were outgased in a vacuum system with a residual pressure of less than 3×10^{-4} Torr at ambient temperature.

Table 1
Synthesis condition and the characterization of the materials.

	Surfactant	PEPU (g)	Synthesis temperature (°C)	Pore size (nm)	Morphology
S-12	C_{11}–COOH	0.27	25	3.1	Flake
S-14	C_{13}–COOH	0.29	45	3.6	Sphere
S-16	C_{15}–COOH	0.31	60	4.0	Small particle
S-18	C_{17}–COOH	0.33	60	5.0	Tube-sphere
MCM-41_{12}	C12TAB		25	2.1	
MCM-41_{16}	C16TAB		60	2.9	

3. Results and discussion

SAXRD patterns of these products are depicted in Fig. 1. All the patterns show the peaks in small angle region, testifying the mesoporous structure of these materials. However, only one peak for all the samples suggests that the mesoporous structures are not ordered enough. With the increase of the chain length of the surfactants, the relevant peaks shift to the small angle region, implying the increase of pore sizes [30].

The morphologies of the samples were observed by SEM. Fig. 2 shows typical SEM images of S-12, S-14, S-16, and S-18. From Fig. 2a, S-12 displays flaky morphology with the average thickness of 200 nm. The morphology of S-14 (Fig. 2b) is a regular sphere with the particle size of about 250 nm. S-16 shows nanoparticles of about 50 nm in size. The nanoparticles agglomerate seriously, because of the small size, as shown in Fig. 2c. The rod-like particles of 2–5 μm in length and 300 nm in diameter can be found from S-18 (Fig. 2d). Interestingly, there is a layer of spheres with the diameter of 200 nm surrounding the rod. Each rod with the spheres around looks like a string of beads.

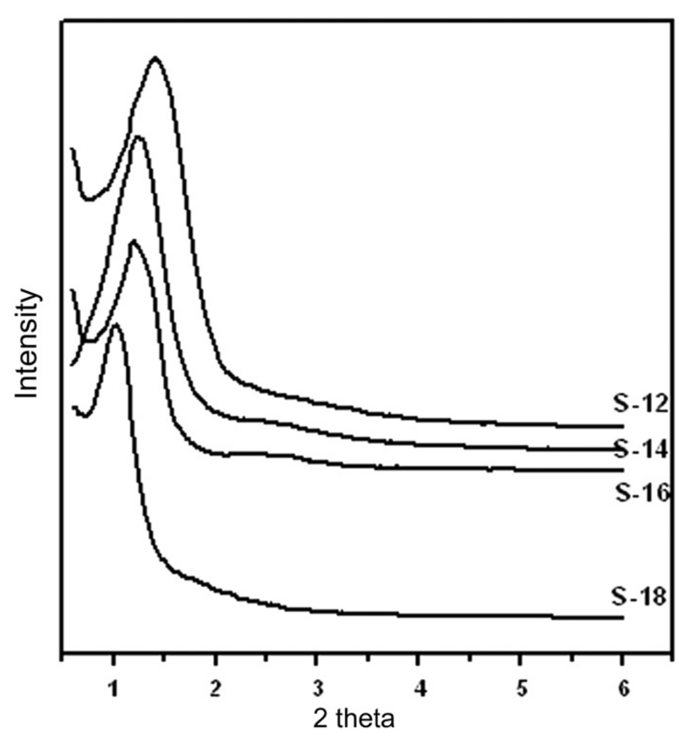

Fig. 1. SAXRD patterns of S-12, S-14, S-16, and S-18.