Direct synthesis of functionalized mesoporous silica by non-ionic alkylpolyethyleneoxide surfactant assembly

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The co-condensation of tetraethoxysilane (TEOS) and organotrialkoxysilane [$(RO)_3SiR'$] assembled in the presence of structure-directing non-ionic polyethyleneoxide surfactant micelles provides a convenient neutral pH synthesis methodology for the one-step preparation of organically functionalized mesostructured materials.

The surfactant-directed synthesis of mesoporous molecular sieves, high surface area metal oxides (800–1400 $m^2 g^{-1}$) with uniform pore sizes (20–100 Å in diameter), have in recent years commanded much attention in the field of materials chemistry.[1–4] Organically functionalized derivatives of such materials were produced by the incorporation or grafting of suitable moieties onto the surface of preformed mesostructured oxides,[5] producing highly effective adsorbents[6,7] and catalysts.[8] Subsequently, an alternate functionalization strategy was reported in which organosilane groups were directly incorporated into the mesostructures by a one-step synthesis procedure,[9–12] allowing the preparation of ordered porous materials with controlled chemical composition by stoichiometric adjustment of the synthesis mixture. Since cationic surfactants were used to prepare these materials, acid leaching was required to remove the templating micelles from the electrically charged frameworks, a treatment which sometimes lead to the structural decomposition of the materials.[11] The use of a non-electrostatic assembly strategy to prepare such functionalized mesostructures may therefore produce an electrostatically neutral framework, allowing the non-destructive removal of the structure-directing surfactant by simple solvent extraction.[13] Here, we report a new synthesis strategy for the one-step preparation of organically functionalized charge-neutral mesoporous silica using non-ionic alkylpolyethyleneoxide surfactants as structure-directing agents, namely Tergitol 15-S-12 [$CH_3(CH_2)_{14}(OCH_2CH_2)_{12}OH$] and Triton-X100 [$(CH_3)_3C(CH_3)_2CCH_2C_6H_4(OCH_2CH_2)_{10}OH$].

The non-functionalized mesostructured silicas MSU-1 and MSU-2 were prepared according to previously published assembly techniques,[4] using Tergitol 15-S-12 and Triton-X, respectively, as structure-directing surfactants. Functionalized derivatives of MSU-1 and MSU-2 were synthesized by stirring TEOS and mercaptopropyltrimethoxysilane (MPTMS) in solutions of Tergitol 15-S-12 (0.02 mol l^{-1}) or Triton-X100 (0.027 mol l^{-1}) at 308 K until clear mixtures formed, then NaF was added (the molar composition of each mixture was 0.1 surfactant: $1-x$ TEOS: x MPTMS:0.02 NaF, where $x = 0$, 0.02 or 0.05). After aging for 24 h, the resulting powders were filtered, air dried and washed by Soxhlet extraction over ethanol for 24 h. The functionalized mesostructures assembled using Tergitol-15-S-12 were thus labeled as MP-MSU-1-2% ($x = 0.02$) and MP-MSU-5% ($x = 0.05$), while those prepared from Triton-X100 were designated as MP-MSU-2-2% ($x = 0.02$) and MP-MSU-5% ($x = 0.05$). The mesostructures were characterized by powder X-ray diffraction (XRD), N_2 sorptometry, elemental analysis (for S), ^{29}Si MAS-NMR and scanning electron microscopy (SEM). The materials' physical properties obtained from these techniques are given in Table 1.

The low angle powder XRD patterns of the MSU-1 and MSU-2 materials featured dominant first order (d_{100}) diffraction peaks (with *d*-spacings of 51 and 66 Å, respectively, see Table 1) and broad, low intensity second order (d_{200}) peaks at higher incidence angle. These represent features typical of ordered mesostructured oxides with 'wormlike' pore channel structures, as expected of materials assembled using either neutral[2] or non-ionic surfactants.[3,4] As organosilane moieties are incorporated into the mesostructures, the d_{100} peaks of the materials become shifted to higher diffraction angles, indicating progressive contractions of the lattice *d*-spacings upon functional group loading (Table 1). Although this effect is slight for the MP-MSU-1 mesostructures (a contraction of only 6% from MSU-1 to MP-MSU-1-5%), significant contraction of the MSU-2 lattice is observed (by 39% from MSU-2 to MP-MSU-2-5%). Moreover, the intensities of the (100) peaks for the functionalized materials were lower in intensity compared to their respective parent mesostructures, and the higher order (200) reflections are no longer detected. Lypophilic interactions between the organosilane molecules and the hydrophobic core of the micelles are likely to result in the deeper penetration of the organosilane molecules within the micelle than do the TEOS molecules. This will cause the micelle structure to 'open-up' and allow TEOS molecules to migrate deeper within the micelle, where they subsequently crosslink with the organosilane functionalities. The perturbations thus caused to the micelle organization thus results in the assembly of more disordered materials with shorter lattice spacings.

The N_2 adsorption isotherms of MSU-1 [Fig. 1(a)] and MSU-2 [Fig. 1(b)] both featured well resolved inflexions at partial pressures between 0.3 and 0.6, demonstrating the existence of uniform mesopore channels with diameters of 32 Å [Fig. 1(c)] and 41 Å [Fig. 1(d)], respectively. No appreciable hysteresis loops were observed in any of the isotherms' desorption

Table 1 Physical characteristics of mesostructures and their functionalized derivatives

Sample	d_{100} lattice spacing/Å	BET surface area/$m^2 g^{-1}$	Pore diameter/Å[a]	S content/ mmol g^{-1}	Organosilane content (%)[b]
MSU-1	51	1225	32	0	0
MP-MSU-1-2%	50	943	26	0.40	2.6
MP-MSU-1-5%	48	858	22	0.87	5.8
MSU-2	66	1018	41	0	0
MP-MSU-2-2%	50	1176	27	0.47	3.0
MP-MSU-2-5%	40	763	—	1.1	7.7

[a] Measured using the Horvath–Kawazoe pore size distribution model.[14] [b] Percentage of Si atoms present as organosilane with respect to total Si content.

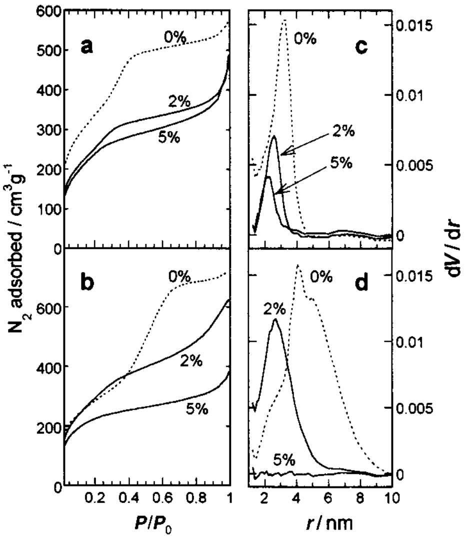

Fig. 1 Left: N_2 adsorption isotherms of (a) MSU-1 (dotted curve) and MP-MSU-1 materials (solid curves), and of (b) MSU-2 (dotted curve) and MP-MSU-2 materials (solid curves). Right: background-substracted Horvath–Kawazoe pore diameter (r) distribution[14] of (c) MSU-1 (dotted curve) and MP-MSU-1 materials (solid curves), and of (d) MSU-2 (dotted curve) and MP-MSU-2 materials (solid curves).

branches, denoting the absence of bottlenecking in the pore channels. The surfactant extraction technique was thus effective in removing the surfactant from the pore channels without damaging the structure of the synthesized materials. The large BET surface areas measured were likewise consistent with the presence of highly porous materials (Table 1). The isotherms of the functionalized derivatives MP-MSU-1-2% [Fig. 1(a)] and MP-MSU-2-2% [Fig. 1(b)] were also indicative of mesoporosity, but the shifts observed in the positions of the inflexions (to between 0.1 and 0.3) show that constrictions in the pore channels have arisen. This can be attributed to both the lattice contractions and to the presence of the mercaptopropyl (MP) moieties which line the pore channel walls, thus reducing the pore diameters and volumes of the mesostructures [Fig. 1(c) and (d)]. Despite pore constriction, the functionalized materials nonetheless retained the very high surface areas characteristic of mesoporous molecular sieves (Table 1). The isotherms of the increasingly loaded MP-MSU-1-5% and MP-MSU-2-5% mesostructures demonstrated an even greater constriction of the pores (Table 1), resulting in further reduction of total pore volume in MP-MSU-1-5% [Fig. 1(c)] and no discernable porosity in MP-MSU-2-5% [Fig. 1(d)]. The significant decreases in surface areas for both of these materials (Table 1) further substantiate these observations. Since all of the functionalized materials are shown to exhibit crystallographic ordering according to their XRD patterns, the incremental featurelessness observed in their N_2 isotherms can be explained by the influence of the increasing amounts of mercaptopropyl groups lining the framework channels, disrupting the uniformity of the pores and reducing their diameters.

The SEM images of the materials revealed aggregates of ultrafine spherical particles with a ‘cotton ball’-like morphology. The particles appeared to be quite uniform in size, with diameters averaging about 0.3 μm for all compositions. The minute sizes of these particles creates significant textural porosity within the mesostructure aggregates, resulting in notable sloping of the nitrogen adsorption curves beyond the mesopore inflexions, as well as significant nitrogen uptake observed at relative pressures approaching unity [Fig. 1(a) and 1(b)].

The ^{29}Si MAS NMR spectra of the functionalized mesostructured (recorded with a 600 s pulse delay) denoted the presence of the following Si sites: Q^4 signals at -110 ppm [$(SiO)_4Si$], Q^3 signals at -101 ppm [$(SiO)_3SiOH$] (both corresponding to framework silica derived from hydrolyzed TEOS), and T^2 and T^3 signals (at -60 and -65 ppm, respectively) corresponding to the organosilane (mercaptopropylsilane) silicon atoms.[11] In all cases, the Q^4/Q^3 signal intensity ratios were close to 1.5, while the intensities of the T^2 and T^3 signals increased as a function of organosilane loading in the materials. By comparing the integrations of these NMR signals, in combination with the elemental analysis results (for S content), the functional group content in the mesostructures was deduced and expressed in Table 1 both in terms of S content and organosilane percentage. Although the amount of organosilane incorporated into the MP-MSU-1 materials was found to be close to that expected on the basis of the stoichiometry of the solution reaction mixture, the functional group loading in MP-MSU-2-2% and MP-MSU-2-5% exceeded this content by a factor of *ca.* 1.5 (Table 1). This suggests that preferential assembly of the organosilane molecules has occurred at the interface of the Triton-X micelles, denoting a greater attraction of the organosilane molecules to the surfactant’s hydrophobic chain.

The one-step preparation of functionalized mesoporous silica by non-ionic surfactant assembly presents a clear advantage over methodologies involving charged quaternary ammonium surfactants, namely that it does not necessitate the use of potentially destructive acid leaching to remove the framework-bound surfactant from the mesostructures. Moreover, the assembly process described in this paper is achieved under neutral pH conditions, unlike the other direct-synthesis approaches which were performed in alkaline environments.[9–12] This feature connotes the possibility of incorporating organic functionalities that would be unstable or otherwise reactive under non-neutral pH conditions, such as strongly electrophilic functionalities. For example, we have preliminary experimental evidence which demonstrates the successful incorporation of chloroalkyl functionalities into mesostructured frameworks following the synthetic protocol described in this paper.

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