A novel anionic surfactant templating route for synthesizing mesoporous silica with unique structure

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Anionic surfactants are used in greater volume than any other surfactants because of their highly potent detergency and low cost of manufacture. However, they have not been used as templates for synthesizing mesoporous silica. Here we show a templating route for preparing mesoporous silicas based on self-assembly of anionic surfactants and inorganic precursors. We use aminosilane or quaternized aminosilane as co-structure-directing agent (CSDA), which is different from previous pathways[1–10]. The alkoxysilane site of CSDA is co-condensed with inorganic precursors; the ammonium site of CSDA, attached to silicon atoms incorporated into the wall, electrostatically interacts with the anionic surfactants to produce well-ordered anionic-surfactant-templated mesoporous silicas (AMS). These have new structures with periodic modulations as well as two-dimensional hexagonal and lamellar phases. The periodic modulations may be caused by the coexistence of micelles that differ in size or curvature, possibly owing to local chirality. These mesoporous silicas provide a new family of mesoporous materials as well as shedding light on the structural behaviour of anionic surfactants.

Mesoporous material syntheses rely on surfactant (S) micelles as templates for the assembly and subsequent and/or simultaneous condensation of inorganic precursors (I)[1,2]. The well-ordered mesoporous silicas (M41S family and SBA-1, 2, 3, 7, and so on) were prepared by using cationic quaternary ammonium surfactants based on electrostatic interaction S^+I^- and $S^+X^-I^+$ pathways[3,4]. The hydrogen-bonding interaction S^0I^0 (HMS family)[5,6] and $(S^0H^+)(X^-I^0)$ (SBA-11, 12, 15, 16 and FDU-1, 2, 5)[7,8] pathways were used to prepare mesoporous silicas with neutral non-ionic surfactants. Although anionic surfactants were used to direct the self-assembly of cationic and anionic metal oxide species through S^-I^+ and $S^-M^+I^-$ (metal counterion mediated) ion pairs, they have
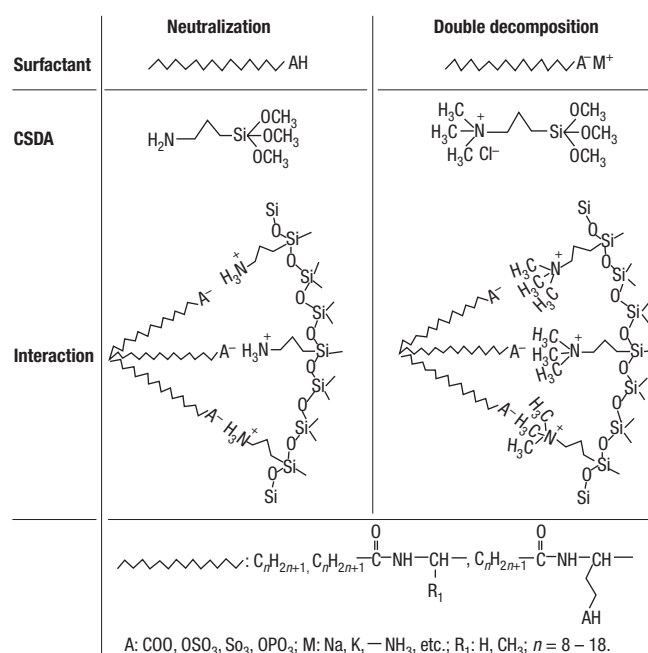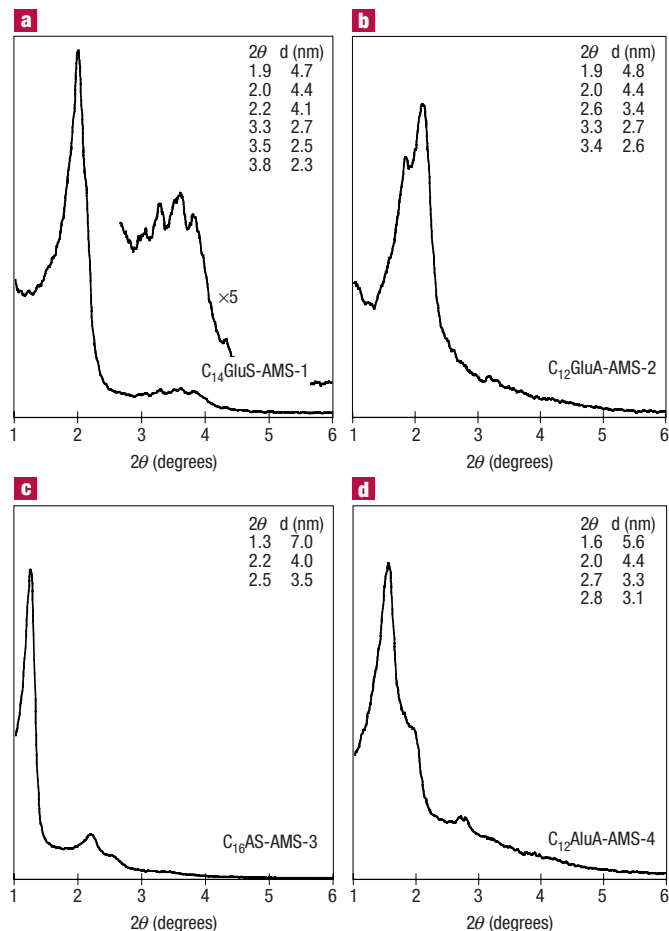

Figure 1 **Schematic illustration of the two types of interactions between aminogroups and anionic surfactant head groups.** The two types of interaction are achieved through neutralization of acid with primary aminosilane APS, and double decomposition of negatively charged anionic salt surfactant with positively charged quaternized aminosilane TMAPS.

A: COO, OSO₃, So₃, OPO₃; M: Na, K, —NH₃, etc.; R₁: H, CH₃; $n = 8 – 18$.

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Figure 2 XRD patterns of calcined AMS-*n* mesoporous silica. The chemical molar composition of the reaction mixture was as follows. **a**, C$_{14}$GluS-AMS-1, C$_{14}$GluS:TMAPS:TEOS:H$_2$O 1:2:10:2,405 (at 100 ºC for 3 d); **b**, C$_{12}$GluA-AMS-2: C$_{12}$GluA:APS:TEOS:H$_2$O 1:2.5:18.5:1,905 (at 100 ºC for 2 d); **c**, C$_{16}$AS-AMS-3: C$_{16}$AS:TMAPS:TEOS:H$_2$O 1:1:9:1,544 (at 60 ºC for 1 d) and **d**, C$_{12}$AlaA-AMS-4, C$_{12}$AlaA:APS:TEOS:H$_2$O 1:0.75:7.5:1,505 (at 60 ºC for 1 d).

2θ	d (nm)
1.9	4.7
2.0	4.4
2.2	4.1
3.3	2.7
3.5	2.5
3.8	2.3

×5

C$_{14}$GluS-AMS-1

2θ	d (nm)
1.9	4.8
2.0	4.4
2.6	3.4
3.3	2.7
3.4	2.6

C$_{12}$GluA-AMS-2

2θ	d (nm)
1.3	7.0
2.2	4.0
2.5	3.5

C$_{16}$AS-AMS-3

2θ	d (nm)
1.6	5.6
2.0	4.4
2.7	3.3
2.8	3.1

C$_{12}$AluA-AMS-4

mostly resulted in lamellar phases[4]. Disordered hexagonal and/or layered non-silica mesoporous materials have been synthesized through the covalent-bond interaction between the inorganic precursors and anionic surfactants[9,10]. It has been reported that anionic surfactants can be used as co-surfactants in the cationic surfactant templating system[11,12].

Anionic salt surfactants (carboxylate, sulphate, sulphonate, phosphate and so on) are widely produced and consumed in vast quantities because of their high detergency and low cost. Various long-chain alkyl acids (fatty acid, *N*-acylaminoacid, sulphuric acid, phosphoric acid and so on) are anionic surfactants when one or two of the acid moieties are neutralized with mono- or polyvalent cationic species such as metal ions, or inorganic and organic ammonium ions. These anionic surfactants are available in a great variety of structures and are mild to humans and the environment, as they are biodegradable and obtained from sustainable resources[13]. In particular, *N*-acyl-L-glutamic acid and *N*-acyl-L-alanine are chiral organic molecules that might prove useful in synthesizing mesoporous materials with chirality. So far, however, these anionic surfactants have not been used in the synthesis of mesoporous silica.

Here we report an anionic surfactant templating route to mesoporous silica that differs from the previous pathways. An organoalkoxysilane with quaternary ammonium organic group (*N*-trimethoxylsilylpropyl-*N*,*N*,*N*-tributylammonium) has been used as the structure-directing agent of zeolites ZSM-5 and ZSM-11[14]. Our approach is based on the co-structure-directing effect imparted with aminosilane or quaternized aminosilane. We demonstrate this effect by using 3-aminopropyltrimethoxysilane (APS) or *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (cation denoted here as TMAPS) (Fig. 1). The negatively charged head group of the anionic surfactant interacts with the positively charged ammonium site of APS and TMAPS electrostatically, through neutralization of the various acids (pK$_a$ = 2–6) and APS

Table 1 Synthesis conditions and mesophases obtained.

Surfactant* Acid	Gel composition†		pH value	Mesophase
	APS/surfactant	Si/surfactant		
C$_{12}$GluA, C$_{14}$GluA,	2–8	15–20	8.9–9.5	AMS-2
C$_{18}$GluA, C$_{12}$AlaA, C$_{14}$AlaA, C$_{12}$GlyA, C$_{14}$GlyA, C$_{16}$GlyA, C$_{12}$AA, C$_{14}$AA	1–8	7.5–12	8.8–10.2	AMS-3
C$_{12}$AlaA	0.75–1	6–7.5	9.2–9.4	AMS-4
C$_{12}$-C$_{14}$AlaA, C$_{12}$-C$_{16}$GlyA, C$_{12}$-C$_{16}$AA	1	3–5	~9.4	AMS-5

Sodium salt	TMAPS/surfactant	Si/surfactant		
C$_{12}$GluS, C$_{14}$GluS,	2	15	8.9–9.5	AMS-1
C$_{12}$AlaS, C$_{12}$GlyS, C$_{12}$AS	1	7.5	8.9–9.5	AMS-2
C$_{16}$GluS, C$_{18}$GluS, C$_{14}$GlyS, C$_{16}$GlyS, C$_{12}$AlaS, C$_{14}$AlaS, C$_{14}$AS, C$_{16}$AS	1	7.5	8.5–9.5	AMS-3

*C$_x$XY
  — A: Free acid, S: Sodium salt
  — Glu: L-Glutamic acid, Gly: Glycine, Ala: L-Alanine
  — C$_n$H$_{2n-1}$O (C$_{12}$H$_{23}$O: *N*-Lauroyl, C$_{14}$H$_{27}$O: *N*-Myristoyl, C$_{16}$H$_{31}$O: *N*-Palmitoryl, C$_{18}$H$_{35}$O: *N*-Stearoyl)

C$_x$AX
  — AA: Free acid, AS: Sodium salt
  — C$_n$H$_{2n-1}$(C$_{12}$H$_{25}$: Lauric, C$_{14}$H$_{29}$: Myristic, C$_{16}$H$_{33}$: Palmitic)

†The well-ordered AMS-*n* silicas were synthesized with 1.0 wt% surfactants at 60 ºC for 1 day.
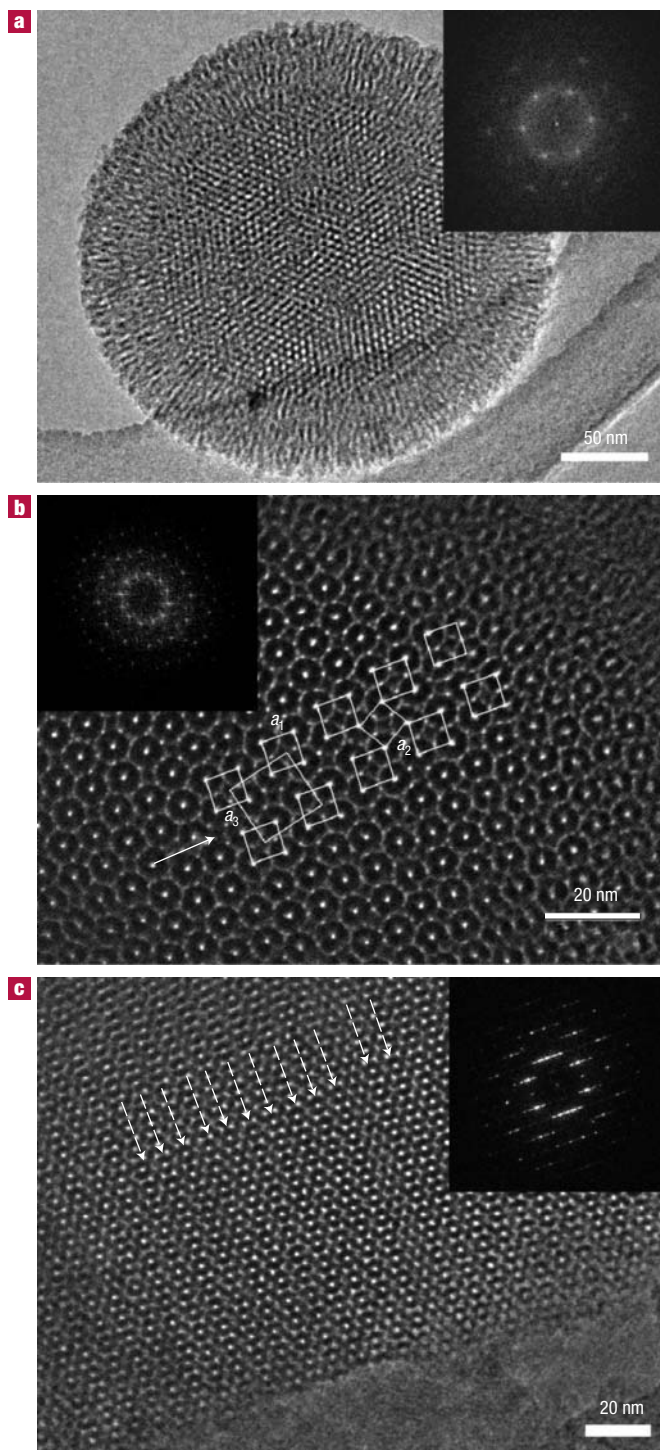
Figure 3 HRTEM images and corresponding Fourier diffractograms of calcined AMS-*n* mesoporous silica shown in Fig. 2. **a**, C_{14}GluS-AMS-1, **b**, C_{12}GluA-AMS-2 and **c**, C_{12}AlaA-AMS-4. (See text for further discussion.)

This templating route produced well-ordered structures that have never previously been reported. The mesostructures possessed uniform pore diameters ranging from 2.0 to 6.2 nm. In Table 1, we list the typical anionic surfactants in the form of carboxylic acid and their salts, the corresponding CSDA, synthesis conditions and mesophases obtained. We have synthesized well-ordered AMS-*n* silicas in the pH range 8.5–10.2 resulting from the appropriate molar ratio of CDSA/anionic surfactant. Obviously, the effective head-group area of the anionic surfactants decreases in the following order: *N*-acylglutamate > *N*-acylalanate > *N*-acylglycinate ≈ carboxylate. The overall topology of the mesostructure is determined by the geometry of the surfactant including chain length and head-group area. We have found TMAPS with a large head-group effective in forming the higher-curvature mesophases. Sulphuric and phosphoric acids and their salt anionic surfactants also led to ordered mesostructures in combination with either APS or TMAPS. Combining sodium salts of anionic surfactants with APS, or amino acids with TMAPS, resulted in disordered mesoporous silicas.

Figure 2a shows the X-ray diffraction (XRD) pattern of calcined AMS-1 mesoporous silica (denoted as C_{14}GluS-AMS-1) synthesized with C_{14}GluS surfactant and TMAPS. Three peaks were observed in the range $2\theta = 1.5–3°$ and an additional three weak peaks in the range $3.5°$ to $6°$. These peaks can be indexed either by the cubic phase with unit cell parameter $a = 7.6 \pm 0.4$ nm or by the 3D-hexagonal phase with unit cell parameters $a = 5.4 \pm 0.4$ nm and $c = 8.8 \pm 0.4$ nm. In the latter case, the c/a ratio is 1.65, which is close to the ideal c/a ratio of 1.633 for the h.c.p. structure of hard spheres. Figure 3a shows a high-resolution transmission electron microscope (HRTEM) image of calcined C_{14}GluS-AMS-1. This material shows a uniaxial cylindrical disc (although some edges can be observed). Channels both perpendicular and parallel to the particle surface can be observed, and Fourier diffractograms suggest the presence of large ordered regions. The corresponding electron diffractogram (inset) is commensurate with 3D-hexagonal symmetry. It is interesting that the particle was surrounded by a layer of different orientation from the inner one, which may block the inner pore system and lead to a decrease in the surface area and pore volume (Table 2).

The XRD pattern of calcined AMS-2 mesoporous silicas (denoted as C_{12}GluA-AMS-2) synthesized by using C_{12}GluA and APS is shown in Fig. 2b. This sample has two well-resolved sharp XRD diffraction peaks in the region of $2\theta = 1.5–3.0°$; as the ratio of d-spacings of the two peaks is close to $2/\sqrt{5}$, these might be indexed to the 200 and 210 reflections ($a = 9.6 \pm 0.4$ nm), based on the cubic system. The HRTEM image (Fig. 3b) reveals a clear arrangement of white dots over very large areas, indicating that the crystal is a well-ordered mesostructure. At this incidence [100] of electrons, the contrast in the two different squares (a_1 and a_2) in Fig. 3a is very similar to that of SBA-1 or SBA-6 (space group: $Pm\bar{3}n$, hereafter SBA-1 type) and we may speculate that the structures in the squares are related to the 3D-cubic SBA-1 structure[15]. It is clear from the arrangement of squares that neighbouring squares are displaced by a half (these have been highlighted by white a_1 squares in the image). This displacement is periodic, suggesting that a new structure with lattice constant a_3 is formed with a different stabilization mechanism from that for structures of the SBA-1 type. The constants a_1, a_2 and a_3 are 6.9 ± 0.2 nm, 6.8 ± 0.2 nm and 14.2 ± 0.2 nm, respectively. None of these values agrees with our simple speculation from powder XRD, $a = 9.6 \pm 0.4$ nm. This type of structural modulation has never been reported.

($pK_b \approx 3.4$), and double decomposition of the anionic surfactant salt and TMAPS quaternary ammonium salt, respectively (Fig. 1). The alkoxysilane sites of APS and TMAPS are co-condensed with tetra-alkoxysilane, for example tetraethoxysilane (TEOS), to be assembled subsequently to form the silica framework. The trimethylene groups of the APS and TMAPS covalently tether the silicon atoms incorporated into the framework to the cationic ammonium groups. The proper molar ratio of CSDA to anionic surfactant should result in a system pH that is favourable for the condensation of alkoxysilane. Either secondary or tertiary aminosilane ($pK_b \approx 3.2–4.2$) can be substituted for APS.

Table 2 Properties of AMS mesoporous silicas synthesized by anionic surfactant templating.

Structure	Surfactant and CSDA	Unit cell* (nm)	Surface area† (m² g⁻¹)	Pore diameter‡ (nm)	Wall thickness (nm)
AMS-1 (3D-hexagonal)	$C_{14}GluS$, TMAPS	$a = 5.4, c = 8.8$	501	2.3	
AMS-2 (3D-cubic)	$C_{12}GluA$, APS	9.6	963	2.8	
AMS-3 (2D-hexagonal)	$C_{16}AS$, TMAPS(ex)§	8.1 (9.2)	387 (311)	5.2 (6.2)	2.9 (3.0)
AMS-4 (bicontinuous 3D-cubic)	$C_{12}AlaA$, APS	13.1	760	4.0	

*Calculated from the XRD patterns
†Calculated by the BET method
‡Calculated from the adsorption branch of the N_2 isotherm by the BJH method
§Extracted sample

When longer-chain surfactants were used for the synthesis, we obtained 2D-hexagonal *p6mm* mesostructures (AMS-3) with a lower curvature, analogous to MCM-41. A typical XRD pattern of the sample (denoted as $C_{16}AS$-AMS-3) synthesized by using $C_{16}AS$ with TMAPS is shown in Fig. 2c. It has been confirmed by electron microscope observations (not shown) that this sample is 2D.

The monovalent acylaminoacid $C_{12}AlaA$ resulted in a 3D-cubic phase ($C_{12}AlaA$-AMS-4) at an APS/$C_{12}AlaA$ molar ratio of 1.0 (Fig. 2d). Figure 3c shows an HRTEM image taken along a high-symmetry zone axis, showing clear structural modulations at the places indicated by arrows. This modulation is described as follows: pairs of bright dots, perpendicular to the arrows, form stripes parallel to the arrows. Neighbouring stripes are displaced randomly with respect to each other by a value of less than half the unit cell distance. This does not cause density modulation but phase modulation perpendicular to the arrows. The modulation (superlattice) causes many fine spots to appear, the separation of which corresponds to the inverse of the distance between the arrows, in the direction perpendicular to the arrows except on the line through the origin of the Fourier diffractogram pattern (Fig. 3c inset). This type of modulation has also never been reported.

A lamellar mesophase (AMS-5) was obtained from the surfactant synthesis systems C_{12}–$C_{14}AlaA$, C_{12}–$C_{16}GlyA$ and C_{12}–$C_{16}AA$ at high surfactant concentrations and low Si/surfactant molar ratios.

AMS-1, 2 and 4 silicas synthesized with chiral surfactants show unique structures with periodic modulations or unusual long-range periodicity. We consider that these modulations may be caused by the coexistence of micelles that differ in size and curvature, possibly including local chirality, suggesting that more than one competing stabilization mechanism is operative, and that more than one synthetic/mechanistic parameter is involved. The formation of different micelle sizes and curvatures can be explained in terms of the interaction of the surfactant molecule tails with APS, considering that ASM-2 and ASM-4 with periodic modulation were synthesized with APS. We have found that AMS-*n* silicas synthesized by using C_nGlyA or C_nGlyS never show periodic modulations. Thus the apparently slight difference in the amino acid structure between $C_nGlyA(S)$ and $C_nAlaA(S)$ surfactants could be decisive, which would provide circumstantial evidence for the possible effect of local chirality. The synthesis mechanism is currently being studied by combining HRTEM image contrast patterns.

All samples with a high-periodicity mesostructure as suggested from XRD patterns show type-IV isotherm. All AMS-*n* samples have sharp capillary condensation steps in the nitrogen adsorption isotherm, and consequently, narrow mesopore size distributions (see Supplementary Information, Fig. S1). The structural properties of the mesoporous silicas are listed in Table 2. The pore diameter and wall thickness are in the ranges 2.0–6.2 nm and 2.4–3.1 nm (not all shown), respectively.

The ²⁹Si NMR spectrums of extracted $C_{16}AS$-AMS-3 silica have been measured (see Supplementary Information, Fig. S2). We observe a peak at –63 p.p.m., attributed to a silicon atom that is bonded to carbon ($T^n = \equiv Si$—$C\equiv$)[16], and peaks at –84, –100 and –110 p.p.m., attributed to Q^2, Q^3 and Q^4 silicons ($Q^n = Si(OSi)_n(OH)_{4-n}$), respectively. We conclude that the silicon atom in the aminosilane is located within the framework by co-condensation with TEOS. After calcinations of AMS-3 silica in air at 650 ºC, the ²⁹Si NMR spectrum shows no resonance of T^n and the Q^3/Q^4 ratio is decreased.

Attempts to prepare mesoporous silica either by using simple primary, secondary or tertiary alkylamines in place of APS, or by using simple quaternary ammonium salts in place of TMAPS, in combination with TEOS, were not successful. These results demonstrate the effectiveness of the strategy of using silanes with pendant amino or quaternized amino as CSDA to initiate silica condensation at the surface of self-organized anionic surfactants.

This choice of CSDA has led to the first successful synthesis of mesoporous silica with anionic surfactants, promising to provide new families of mesoporous materials from a large variety of anionic surfactants. Mesoporous materials synthesized in this way show structural periodicity arising from modulations occurring along specific orientations. We believe that the latter is a new structural characteristic of mesoporous materials that arises directly as a result of the anionic surfactant assembling process. This could open up new uses for mesoporous silica in applications such as catalysis, adsorption and separations, nanocasting and nanodevices.

METHODS

MATERIALS SYNTHESIS

In a typical synthesis, a mixture of 4.16 g TEOS and 1.03 g TMAPS (50% in methanol) was added to a mixture of 0.56 g of $C_{16}AS$ (for the surfactant abbreviations, see Table 1) and 56 g of deionized water with stirring at 60 ºC. After the mixture has been stirred for 24 h, the mesostructured product formed was cured at 100 ºC for 1–3 days. The products were filtered and dried at 60 ºC. The anionic surfactants were removed by exhaustive solid–liquid extraction using 15 vol.% H_2O/ethanol solutions at boiling temperature overnight to give the mesoporous materials with pendant amino or ammonium groups. Both the anionic surfactants and the organic portions of the CSDA used were removed by calcination at 650 ºC for 6 h.

MEASUREMENTS

XRD patterns were recorded on an MX Labo powder diffractometer equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 1.0 deg min⁻¹ over the range 1.5–10.0º (2θ). HRTEM images were taken on a JEM-3010 microscope operating at an accelerating voltage of 300 kV. The N_2 adsorption–desorption isotherms were measured at –196 ºC on a Belsorp 28SA sorptionmeter. The cross polarization ²⁹Si NMR spectra were collected at a JEOL-LA400WB 400 MHz spectrometer at 79.4 MHz and a sample spinning frequency of 5 kHz.

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Competing financial interests

The authors declare that they have no competing financial interests.