A hybrid mesoporous material with uniform distribution of carboxy groups assembled from a cubic siloxane-based precursor†

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A novel hybrid mesoporous material functionalized with carboxy groups was synthesized by self-assembly of a novel building block consisting of a cubic siloxane unit and a long organic chain with an ester bond and the following hydrolysis of ester bonds, representing a promising approach to designing hybrid structures at both molecular and mesoscopic scales.

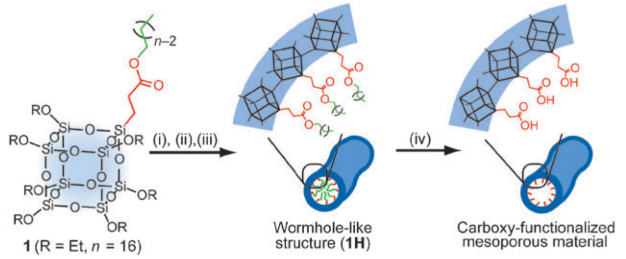
Organically-functionalized mesoporous silicas have received increasing interest from both scientific and technological viewpoints. Such materials are generally produced by post-modification of mesoporous silica or by co-condensation of organoalkoxysilanes and tetraalkoxysilanes in the presence of surfactants.[1] Fine control of the local structure, in particular, the configuration and distribution of the organic groups on the pore surface, is crucial for their use in advanced applications in separation and catalysis.[2] However, achieving such control still remains a great challenge. A promising approach to overcome this difficulty should be the use of well-defined, functionalized molecular building blocks capable of self-assembly.[3,4]

We have recently demonstrated the direct formation of various hybrid mesostructures from precursors consisting of an alkyl chain and alkoxysilyl groups.[5,6] This approach relies on the surfactant-free self-assembly of amphiphilic hydrolyzed species and subsequent polycondensation. Most recently, we have reported the design of monoalkyl-substituted cubic siloxanes ($C_nH_{2n+1}Si_8O_{12}(OEt)_7$, $n = 16$–20) and their self-assembly into two-dimensional (2D) hexagonal hybrids.[7] Because of the rigid cubic siloxane unit, hydrolysis and polycondensation of the constituent alkoxy groups proceeded with the retention of the original cage structure, allowing the design of hybrid structures at both the molecular and mesoscopic scales. However, these self-assembled hybrids have no porosity, and the generation of pores requires calcination at high temperature, *i.e.*, by complete elimination of the organic moieties accompanied by thermal rearrangement of the siloxane networks.

Herein, we report a novel building-block approach to produce functionalized mesoporous materials using a cubic siloxane-based precursor bearing an alkylester group (**1** in Scheme 1). Self-assembly of the hydrolyzed species followed by polycondensation and cleavage of ester bonds led to the successful synthesis of hybrid mesoporous silica consisting of siloxane cages bearing carboxyethyl groups (Scheme 1). The defined proportion and truly uniform distribution of carboxy groups (laterally separated from each other by at least two SiO_4 units) on the pore walls would be useful for highly effective and selective adsorption of bio-related molecules by specific interactions and also as scaffold for further chemical modifications. This strategy is also important for the future design of innovative catalysts with a high degree of site isolation.

Precursor **1** was synthesized by Pt-catalyzed hydrosilylation of hexadecylacrylate ($C_{16}H_{33}OC(O)CH{=}CH_2$) with $H_8Si_8O_{12}$,[8] followed by conversion of seven SiH groups into SiOEt groups.[9]‡ Hydrolysis of **1** was performed in a solution with a molar ratio of **1** : THF : H_2O : HCl = 1 : 100 : 35 : 0.5. After stirring at room temperature for 3 days, the hydrolyzed solution was cast onto glass substrates and air-dried at room temperature for 2 days. The silica-based hybrid (**1H**) was obtained as a transparent, thick film, which was scraped off from the substrates, pulverized, washed with hexane, and air-dried before characterization. Hydrolysis of the ester bonds was performed by refluxing **1H** ($\sim$0.3 g) in a mixture of THF (20 mL), conc. HCl (4 mL), and H_2O (1 mL) for 2 days, followed by centrifugation and drying *in vacuo*.

After undergoing hydrolysis for 3 days, liquid-state ^{13}C and ^{29}Si NMR spectra for the precursor solution were recorded. From the intensity ratio of the $CH_3\mathit{C}H_2OSi$ (60.0 ppm) and $CH_3\mathit{C}H_2OH$ (57.7 ppm) signals in the ^{13}C NMR spectrum (Fig. S1 in ESI†), it was estimated that at least 70% of SiOEt groups were hydrolyzed, while the hydrolysis of ester bonds ($-\mathit{C}H_2OC(O)-$, at 65.0 ppm) to form alcohols ($-\mathit{C}H_2OH$, at 62.4 ppm) was relatively low. Hydrolysis of ethoxy groups was also confirmed by ^{29}Si NMR (Fig. S2 in ESI†). Unreacted **1** exhibits four signals, with one corresponding to the T^3



Scheme 1 Synthesis of hybrid mesostructure (**1H**) from a functionalized cubic siloxane-based precursor (**1**) by (i) hydrolysis, (ii) self-assembly, (iii) polycondensation and (iv) hydrolysis of ester bonds.

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($CSi(OSi)_3$) site and three corresponding to inequivalent Q^3 ($Si(OSi)_3(OEt)$) sites. After hydrolysis, the signals due to $(SiO)_3SiOH$ appeared at −100.5 ppm being shifted from those of $(SiO)_3SiOEt$ (at around −102.5 ppm).

Similar to the case of monoalkyl-substituted precursors,[7] no Q^4 signal was observed during hydrolysis of **1**, which is crucial for the present self-assembly process. The formation of siloxane networks was triggered by the evaporation of solvent, as confirmed by the solid-state ^{29}Si MAS NMR spectrum of **1H** (Fig. 1a). Three signals corresponding to the T^3, Q^3 and Q^4 (Q^x, $Si(OSi)_x(OH)_{4-x}$) sites are mainly observed at −64, −99 and −108 ppm, respectively. The appearance of the Q^4 signal indicates the formation of the networks of siloxane cages. From the relative intensity ratio of the Q^4 signal ($Q^4/(Q^2 + Q^3 + Q^4) = 0.36$), the average number of cage corners linked to other cages is calculated to be 2.6 per Si_8O_{12} unit. The low degree of polycondensation is possibly due to the incomplete hydrolysis of SiOEt groups as well as to the rigidity of the cubic siloxane units. These signals are still observed after the acid treatment (Fig. 1b). The increase of the $Q^4/(Q^2 + Q^3 + Q^4)$ ratio from 0.36 to 0.54 after acid treatment suggests that further condensation occurred during this step. However, this increase is much lower than that observed for monoalkyl-substituted cubic siloxanes upon calcination (*i.e.* from 0.39 to 0.78).[7]

The appearance of small Q^2 signals (−90 ppm) in both spectra, and the increased ratio of the T^2 units after the acid treatment are suggestive of the cleavage of Si–O–Si linkages. However, their ratios are very low, implying that the networks of the siloxane cages were retained for the most part. Actually, the FT-IR spectra of **1H** before and after the acid treatment (Fig. S3 in ESI†) show a band at 584 cm^{-1}, which is typically observed for siloxane-based materials containing double-four-membered rings.[10] It should be noted that this band almost disappeared when **1H** was calcined to remove organic moieties (data not shown). This is indicative of the thermal rearrangement of the siloxane networks, being in agreement with that reported for the monoalkyl-substituted precursors.[7]

The mesostructure of **1H** was characterized by XRD and TEM. Fig. 2 (left) shows the powder XRD patterns of **1H** before and after the acid treatment. As-synthesized **1H** exhibits a single broad peak ($d = 4.1$ nm) characteristics of a wormhole-like mesostructure (Fig. 2 (left) (a)). The low structural order might be due to the incomplete hydrolysis of SiOEt groups as well as the partial loss of hydrophobic alkyl tails through the cleavage of ester bonds during the hydrolysis process, as mentioned above. This mesostructure was retained even after the acid treatment as confirmed by XRD (Fig. 2 (left) (b)) and TEM (Fig. 2 right). Importantly, no decrease in the *d* spacing occurred upon acid treatment, which suggests that the shrinkage of the siloxane networks was virtually negligible.

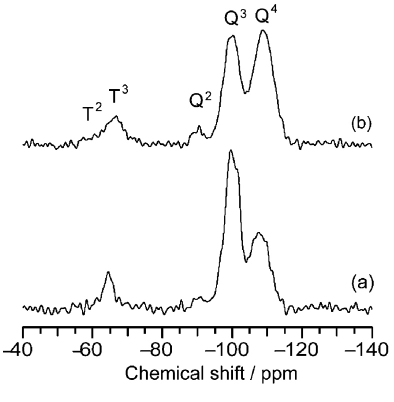

Fig. 1 Solid-state ^{29}Si MAS NMR spectra of **1H** (a) before and (b) after the acid treatment.

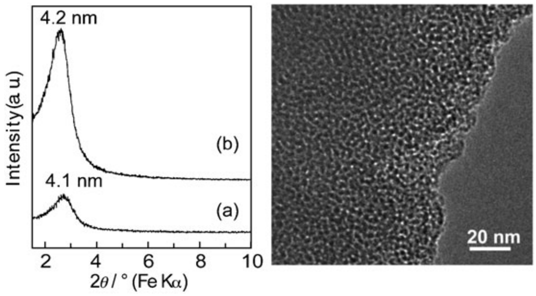

Fig. 2 Powder XRD patterns of **1H**: (a) before and (b) after the acid treatment (left), and a typical TEM image of **1H** after the acid treatment (right).

The removal of alkyl alcohol ($C_{16}H_{33}OH$) from **1H** *via* the hydrolysis of ester bonds ($C_{16}H_{33}OC(O)$–) was confirmed by FT-IR (Fig. S3†). Upon acid treatment, the characteristic bands of C–H stretching modes (2850–3000 cm^{-1}) considerably decreased while the C=O stretching vibration (1720 cm^{-1}) remained intact. Similar results were also obtained by solid-state ^{13}C CP/MAS NNR (Fig. 3). The spectrum before the acid treatment showed the signals corresponding to the $C_{16}H_{33}OC(O)C_2H_4$– groups along with a small signals for residual SiOEt groups. After the acid treatment, the intense signals assigned to the internal methylene carbons of C16 chains (at 30 ppm) almost disappeared, while signals for the carboxyethyl ($HOOC$–C_2H_4–) groups are clearly observed. The residual SiOEt groups were also hydrolyzed, which is consistent with the increase of the Q^4/Q^3 ratio in the ^{29}Si MAS NMR spectrum (Fig. 1b).

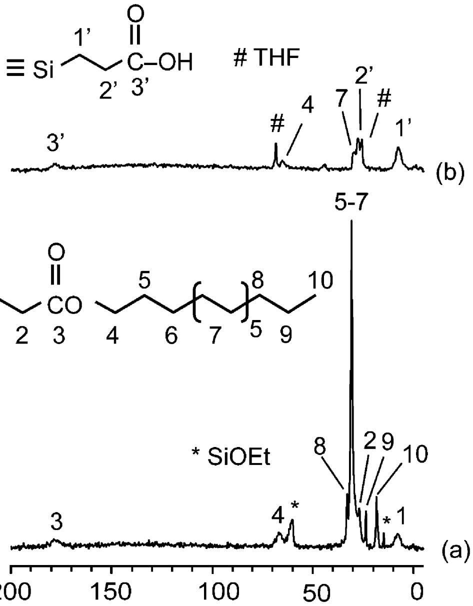

Fig. 3 Solid-state ^{13}C CP/MAS NMR spectra of **1H**: (a) before and (b) after the acid treatment.

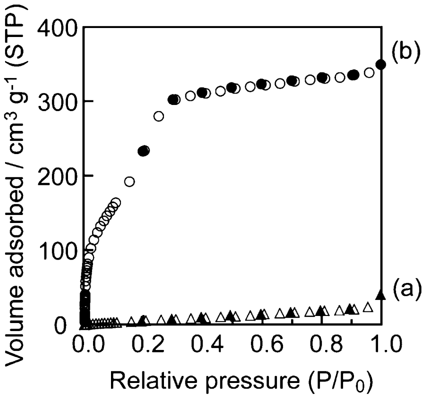

Fig. 4 Nitrogen adsorption–desorption isotherms of **1H** (a) before and (b) after the acid treatment. Open symbols and filled symbols denote adsorption and desorption, respectively.

The nitrogen adsorption measurement revealed that, although the as-synthesized **1H** had a very low BET surface area ($\sim$10 m^2 g^{-1}), mesopores were generated by the acid treatment to remove C16OH (Fig. 4). The BET surface area, pore volume, and NLDFT pore diameter were calculated to be 630 m^2 g^{-1}, 0.48 cm^3 g^{-1}, and 3.3 nm, respectively.[11] It is noteworthy that the pore size is comparable to that of the mesoporous silica prepared by calcination of the hybrid derived from $C_{20}H_{41}Si_8O_{12}(OEt)_7$, having a much longer alkyl chain.[7] This is attributed to the lack of thermal shrinkage of the siloxane networks during the acid treatment, as previously mentioned.

These results demonstrate the successful synthesis of a hybrid mesoporous material with three-dimensionally accessible pores modified with carboxyethyl groups. The C/SiO_2 molar ratio in the sample after the acid treatment was calculated to be $\sim$0.45 (CHN and TG data). This value is slightly higher than the theoretical value for a sample containing one carboxyethyl group per cage (C/SiO_2 = 0.375) but is much lower than the value before the acid treatment (2.375). It is thus estimated that about 97% of alkyl ester groups were hydrolyzed and removed. The density of the carboxyethyl groups on the pore surface can be estimated to be $\sim$1.8 nm^{-2}, assuming that the siloxane cage is hexagonally packed on the pore surface (see Fig. S4 in ESI†).

Previously, there have been several reports on the synthesis of carboxy-functionalized mesoporous materials.[12,13] Zhang *et al.* have reported the synthesis of amino acid-functionalized mesoporous silica *via* cleavage of alkyl ester bonds by an acid treatment.[14] However, all of the previous works relied on the surfactant-directed self-assembly processes involving the co-condensation of organosilanes and tetraalkoxysilanes. In such cases, structural and compositional homogeneities at the molecular level are not ensured because of the differences in the hydrolysis rates of the precursors arising from both inductive and steric effects. The present approach, using single, well-defined precursors, should enable us to create elaborate structures. Considering that the T^3 site was mostly retained in **1H** even after the acid treatment (Fig. 1b), it is plausible that carboxyethylsilyl groups are homogeneously distributed in the pores and more importantly they are laterally separated from each other by at least two SiO_4 units. This type of material design is essential for adsorption and catalytic applications of mesoporous materials.[2,15]

In conclusion, we have demonstrated the direct formation of a novel hybrid mesoporous material by self-assembly of substituted octasiloxane cages. Incorporation of hydrolyzable ester bonds resulted in the formation of a carboxy functionalized mesoporous material without thermal rearrangement of the cubic siloxane units. This approach provides a basis for the construction of hybrid mesostructures with precisely designed structures.

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Notes and references

‡ Hydrosilylation was performed by the addition of a 0.02 M acetonitorile solution of $H_2PtCl_6{\cdot}6H_2O$ (Kanto Kagaku Co., Ltd.) to a mixture of $H_8Si_8O_{12}$, hexadecylacrylate (Tokyo Kasei), and toluene (50 mL per 1 g of $H_8Si_8O_{12}$) present in the molar ratios of $H_8Si_8O_{12}$: hexadecylacrylate : $H_2PtCl_6{\cdot}6H_2O$ = 1 : 1.5 : 1.6 × 10^{-3}, and the mixture was stirred at 50 °C for 1 day under nitrogen atmosphere. The mono-addition product, $C_{16}H_{33}OC(O)C_2H_4(H_7)Si_8O_{12}$, was isolated by gel permeation chromatography (GPC) using chloroform as the eluent (a waxy solid, yield: $\sim$30% based on $H_8Si_8O_{12}$). Note that an increase in the reaction temperature (>60 °C) resulted in the formation of both α- and β-addition products that are difficult to separate. Complete conversion of SiH into SiOEt groups was accomplished using the procedure previously reported by us,[7] giving **1** as a clear, viscous liquid (yields: $\sim$70% based on $C_{16}H_{33}OC(O)C_2H_4(H_7)Si_8O_{12}$).

1 For reviews, see: L. Nicole, C. Boissière, D. Grosso, A. Quach and C. Sanchez, *J. Mater. Chem.*, 2005, **15**, 3598; F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216; S. Fujita and S. Inagaki, *Chem. Mater.*, 2008, **20**, 891.
2 M. W. McKittrick and C. W. Jones, *Chem. Mater.*, 2003, **15**, 1132; K. K. Sharma and T. Asefa, *Angew. Chem., Int. Ed.*, 2007, **46**, 2879; K. K. Sharma, A. Anan, R. P. Buckley, W. Ouellette and T. Asefa, *J. Am. Chem. Soc.*, 2008, **130**, 218.
3 C. Sanchez, G. J. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061.
4 R. E. Morris, *J. Mater. Chem.*, 2005, **15**, 931.
5 A. Shimojima and K. Kuroda, *Chem. Rec.*, 2006, **6**, 53; A. Shimojima, *J. Ceram. Soc. Jpn.*, 2008, **116**, 278.
6 A. Shimojima and K. Kuroda, *Angew. Chem., Int. Ed.*, 2003, **42**, 4057; A. Shimojima, Z. Liu, T. Ohsuna, O. Terasaki and K. Kuroda, *J. Am. Chem. Soc.*, 2005, **127**, 14108.
7 A. Shimojima, R. Goto, N. Atsumi and K. Kuroda, *Chem.–Eur. J.*, 2008, **14**, 8500.
8 P. A. Agaskar, *Inorg. Chem.*, 1991, **30**, 2707.
9 A. R. Bassindale and T. Gentle, *J. Organomet. Chem.*, 1996, **521**, 391.
10 L. Zhang, H. C. L. Abbenhuis, Q. H. Yang, Y.-M. Wang, P. C. M. M. Magusin, B. Mezari, R. A. van Santen and C. Li, *Angew. Chem., Int. Ed.*, 2007, **46**, 5003; Y. Hagiwara, A. Shimojima and K. Kuroda, *Chem. Mater.*, 2008, **20**, 1147.
11 P. I. Ravikovitch, D. Wei, W. T. Chueh, G. L. Haller and A. V. Neimark, *J. Phys. Chem. B*, 1997, **101**, 3671.
12 N. Liu, R. A. Assink and C. J. Brinker, *Chem. Commun.*, 2003, 370; C.-M. Yang, B. Zibrowius and F. Schüth, *Chem. Commun.*, 2003, 1772.
13 L. Han, Y. Sakamoto, O. Terasaki, Y. Li and S. Che, *J. Mater. Chem.*, 2007, **17**, 1216.
14 Q. Zhang, K. Ariga, A. Okabe and T. Aida, *J. Am. Chem. Soc.*, 2004, **126**, 988.
15 W. Otani, K. Kinbara, Q. Zhang, K. Ariga and T. Aida, *Chem.–Eur. J.*, 2007, **13**, 1731.