PMO[KIT-5]-n: synthesis of highly ordered three-dimensional periodic mesoporous organosilicas with *Fm*3*m* symmetry†

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Divalent surfactant $[CH_3(CH_2)_{15}N(CH_3)_2(CH_2)_3N(CH_3)_3]^{2+}$-2Br⁻ ($C_{16-3-1}$) was used as a structure directing agent (SDA) for the synthesis of highly ordered periodic mesoporous organosilicas (PMOs) with cubic *Fm*3*m* symmetry from 1,2-bis(triethoxylsilyl)ethane (BTEE) under basic conditions.

Periodic mesoporous organosilicas (PMOs) are intriguing members of a rapidly growing library of surfactant-templated mesoporous materials.[1,2] Such advanced hybrid inorganic–organic materials can be obtained *via* hydrothermal synthesis from bridged organosilane molecules $(OR)_3Si–X–Si(OR)_3$ [X = functional (metal) organic group] in the presence of cationic,[3–7] anionic,[8] neutral,[9] and non-ionic oligomeric[10–17] surfactants as structure directing agents (SDAs). A wide range of differently charged/shaped SDAs and varied reaction conditions have been employed to achieve topological control of the mesophase. At present, four different PMO pore architectures have been identified on the basis of powder X-ray diffraction (PXRD) and high-resolution transmission electron microscopy (HRTEM). Highly ordered PMOs with cubic *Pm*3*n* symmetry were synthesized by using the routine surfactant $C_{16}H_{33}N(CH_3)_3Cl$ ($C_{16}TAC$) or a binary surfactant mixture ($C_{18}TAC$ and Brij30 [$C_{12}H_{25}$-$(OCH_2CH_2)_4OH$]) as SDAs under basic reaction conditions.[6,7a,18] Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) as an SDA under acidic reaction conditions and the presence of inorganic salts accomplished long-range ordered PMOs with cubic *Im*3*m* symmetry and large cage-like pores (d_p = 9.8 nm).[16a] Correspondingly, hexagonal PMOs with large pore diameters (d_p = ~4.0–10 nm, space group *P*6*mm*) were obtained by using non-ionic triblock copolymers as SDAs under acidic reaction conditions.[10–17] Application of routine SDAs C_nTAC and C_nTAB (n = 16,18) under basic reaction conditions gave PMOs with 2D (*P*6*mm*) or 3D (*P*6_3/*mmc* space group) hexagonal symmetry and pore sizes <5 nm.[3–7] It is noteworthy that the use of divalent surfactants as SDAs to create PMOs has almost been neglected.[18,19] Herein, we wish to report the synthesis of a novel periodic mesoporous organosilica with cubic *Fm*3*m* symmetry (designated PMO[KIT-5]-**n** with [KIT-5][20] representing the topology and **n** the sample number).

We used divalent surfactant C_{16-3-1} [$CH_3(CH_2)_{15}N(CH_3)_2$-$(CH_2)_3N(CH_3)_3]^{2+}2Br^-$ as an SDA and 1,2-bis(triethoxylsilyl)-ethane (BTEE) as an organosilica source to prepare PMO materials with cubic *Fm*3*m* symmetry. In a typical synthesis of PMO[KIT-5]-**1**, a mixture of C_{16-3-1} (3.60 g), NaOH (0.73 g), and warm deionized water (55 g) was stirred to form a clear solution. After the addition of 2.82 g of BTEE, the stirring was continued for 24 h at ambient temperature. Heating this solution at 95 °C for 7 h caused precipitation. The resulting suspension was then aged at 95 °C for 72 h without stirring and the white precipitate was recovered by suction filtration. The as-synthesized PMO was dried in air and the surfactant removed by Soxhlet extraction in hydrochloride-acidified ethanol solution. Complete extraction was confirmed by the disappearance of characteristic IR bands and by the absence of surfactant carbon signals in the solid state ^{13}C NMR spectrum.

The PXRD pattern of the solvent-extracted PMO[KIT-5]-**1** clearly shows four well-resolved diffraction peaks in the 2θ angle range of 1–4° that are indexed as (111), (200), (220), and (311) reflection planes, with interplanar *d* spacings of 5.00, 4.37, 3.11 and 2.70 nm, respectively. This is in accordance with a face-centered-cubic *Fm*3*m* structure (the unit cell parameter of the cubic lattice is 8.66 nm), similar to that reported for the purely siliceous mesoporous material KIT-5.[20] The previously reported purely siliceous mesoporous materials with the *Fm*3*m* space group were also obtained from multicomponent gels under acidic conditions by using nonionic triblock copolymer surfactants as SDAs, inorganic salts (KCl), and/or organic additives.[21–23] To the best of our knowledge, PMOs with face-centered-cubic *Fm*3*m* symmetry have not been reported so far. Scanning electron microscopy (SEM) images of solvent-extracted PMO[KIT-5]-**1** show mostly spherical morphologies of a relatively uniform size of *ca.* 1 μm (see ESI, S1†).

The N_2 adsorption–desorption isotherm for material **1** is of type IV with an H2 hysteresis loop indicating a cage-like mesopore configuration, however, which is not similar to that of previously reported KIT-5 (Fig. 2).[20] Selected physical parameters are listed in Table 1. According to Neimark's calculation method,[24] the cage diameter of PMO[KIT-5]-**1** is *ca.* 5.38 nm.‡

The ^{13}C cross-polarization (CP) MAS NMR spectrum of solvent-extracted material PMO[KIT-5]-**1** shows one signal at 5.5 ppm for the bridging ethylene group of the –$SiCH_2CH_2Si$– moieties (see ESI, S2†). The ^{29}Si MAS NMR spectrum features two signals at −57 and −67 ppm, which are attributed to T^2 [$CSi(OSi)_2OH$] and T^3 [$CSi(OSi)_3$] silicon resonances, respectively (see ESI, S2). Complete cross-linking of the PMO structure *via* Si–C bonds was revealed by the absence of any Q^n [$Si(OSi)_n$-$(OH)_{4-n}$] silicon signals.

Details of the synthesis parameters are shown in Table 2. The divalent surfactant concentration is a key factor in the formation of PMOs with *Fm*3*m* symmetry. As shown for samples PMO[KIT-5]-**2** (**3**, **4** or **5**), a molar ratio of BTEE : C_{16-3-1} = 1 : 0.60 gave highly

ordered materials (Fig. 1 and ESI, S3†). Moreover, decrease of the aging temperature T_{aging} and time t_{aging} caused a considerable increase of BET surface area, pore volume, and cage diameter (Table 1, Fig. 2). TEM analysis of benchmark system **4**, **5** confirmed its high structural order and the absence of any mesophase intergrowths (see ESI, S4†). At lower divalent surfactant concentration (BTEE : $C_{16\text{-}3\text{-}1}$ = 1 : 0.45), a hexagonal mesophase PMO[MCM-41]-**6** of *P6nm* symmetry was formed (Tables 1 and 2, ESI, S5†). For comparison, use of the more common surfactant C_{16}TAB (C_{16}) as an SDA under otherwise identical reaction conditions gave a hexagonal structure, PMO[MCM-41]-**7**, with a *P6mm* space group (Tables 1 and 2, ESI, S6†). In addition, the base concentration drastically affects the formation of PMOs with *Fm3m* symmetry: molar NaOH concentrations of 1.80, 2.60, and 2.80 produced PMOs unequivocally displaying a hexagonal structure (not shown). The
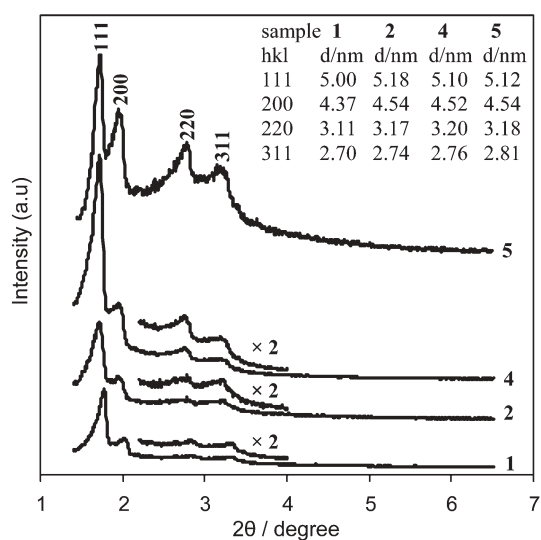
Table 1 Analyzed and calculated parameters of materials **1**–**8**

Sample	$a_s{}^a$/m^2 g^{-1}	$d_{\text{BJH}}{}^b$/nm	V^c/cm^3 g^{-1}	$d_{\text{cage}}{}^d$/nm
PMO[KIT-5]-**1**	500	2.9	0.46	5.38
PMO[KIT-5]-**2**	580	2.9	0.52	5.69
PMO[KIT-5]-**3**	670	2.9	0.61	5.76
PMO[KIT-5]-**4**	750	2.9	0.65	5.78
PMO[KIT-5]-**5**	840	3.0	0.67	5.83
PMO[MCM-41]-**6**	600	2.9	0.54	—
PMO[MCM-41]-**7**	750	2.6	0.57	—
PMO[SBA-1]-**8**	770	3.4	0.69	5.94

^{a} BET surface area. ^{b} BJH (Barrett–Joyner–Halenda) pore diameter calculated from the adsorption branch. ^{c} Total pore volume. ^{d} Cage diameter.[24]

Table 2 Selected synthesis parameters of materials **1**–**8**

Sample	SDA^a	Amount NaOH^a	T_{aging}/°C; t_{aging}/h	Mesophase
PMO[KIT-5]-**1**	$C_{16\text{-}3\text{-}1}$(0.88)	2.35	95; 72	Cubic (*Fm3m*)
PMO[KIT-5]-**2**	$C_{16\text{-}3\text{-}1}$(0.60)	2.35	95; 72	Cubic (*Fm3m*)
PMO[KIT-5]-**3**	$C_{16\text{-}3\text{-}1}$(0.60)	2.35	95; 24	Cubic (*Fm3m*)
PMO[KIT-5]-**4**	$C_{16\text{-}3\text{-}1}$(0.60)	2.35	80; 24	Cubic (*Fm3m*)
PMO[KIT-5]-**5**	$C_{16\text{-}3\text{-}1}$(0.60)	2.35	70; 24	Cubic (*Fm3m*)
PMO[MCM-41]-**6**	$C_{16\text{-}3\text{-}1}$(0.45)	2.35	95; 24	Hexag. (*P6mm*)
PMO[MCM-41]-**7**	C_{16}(0.60)	2.35	80; 24	Hexag. (*P6mm*)
PMO[SBA-1]-**8**	$C_{18\text{-}3\text{-}1}$(0.60)	2.35	80; 24	Cubic (*Pm3n*)

^{a} Molar ratio of divalent surfactant or NaOH and BTEE.

Fig. 1 Powder X-ray diffraction (PXRD) patterns of solvent-extracted materials PMO[KIT-5]-**1**, **2**, **4** and **5**.

sample	**1**	**2**	**4**	**5**
hkl	d/nm	d/nm	d/nm	d/nm
111	5.00	5.18	5.10	5.12
200	4.37	4.54	4.52	4.54
220	3.11	3.17	3.20	3.18
311	2.70	2.74	2.76	2.81

importance of using $C_{16\text{-}3\text{-}1}$ as an SDA for cubic *Fm3m* mesophase control was further corroborated by an experiment employing divalent $C_{18\text{-}3\text{-}1}$ instead of $C_{16\text{-}3\text{-}1}$. This hydrothermal reaction produced a highly ordered cubic mesophase PMO[SBA-1]-**8** with a *Pm3n* space group (see ESI, S7†). Details of the PMO[SBA-1]-**n** materials will be reported soon as part of a full paper.

In summary, divalent surfactant molecules of type $C_{n\text{-}3\text{-}1}$ were found to direct uniquely the formation of PMOs with different symmetry. Accordingly, novel PMOs with a cubic *Fm3m* structure were prepared from BTEE under basic conditions. Both divalent surfactant and base concentration as well as aging temperature and aging time are important factors to govern the mesophase structure.

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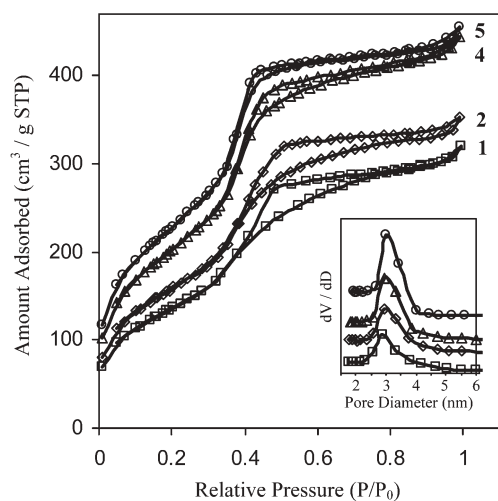*E-mail: reiner.anwander@ch.tum.de; Fax: +49 89 28914374; Tel: +49 89 28913096*

Fig. 2 N$_2$ adsorption–desorption isotherms for solvent-extracted materials PMO[KIT-5]-**1** (**2**, **4** and **5**). The inset shows the pore size distribution calculated by the BJH method (adsorption branch).

Notes and references

‡ For the calculation of d_{cage}, the density ρ_{V} of the organosilica walls was assumed to be that of siliceous materials (2.2 g cm^{-3}).

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