

Ethylene-bridged Mesoporous Organosilicas with Hexagonal and Cubic Symmetry

Yucang Liang^{a,b}, Egil Sev. Erichsen^c, Marianne Hanzlik^d, and Reiner Anwander^{a,b}

^a Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

^b Department of Chemistry, University of Bergen, Allégaten 41, N-5007, Bergen, Norway

^c Laboratory for Electron Microscopy, University of Bergen, Allégaten 41, N-5007, Bergen, Norway

^d Institut für Technische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. Reiner Anwander. Fax: +49(0)7071/29 2436.

E-mail: reiner.anwander@uni-tuebingen.de

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

A series of ordered periodic mesoporous organosilicas (PMOs) with cubic and hexagonal symmetries were fabricated by using divalent surfactants $[\text{CH}_3(\text{CH}_2)_{15}\text{NMe}_2(\text{CH}_2)_3\text{NMe}_3]^{2+} 2\text{Br}^-$ (C_{16-3-1}) or binary surfactant mixtures $[\text{CH}_3(\text{CH}_2)_{15}\text{NMe}_3]^+ \text{Br}^-$ (C_{16}TABr) and C_{16-3-1} as structure-directing agents (SDAs) and 1,2-bis(triethoxysilyl)ethane (BTEE) as an organosilica source under various basic conditions. The shape/structure of surfactant, molar ratio of binary surfactant mixtures, and base concentration crucially affect the formation of distinct mesophases. Face-centered cubic $Fm\bar{3}m$ mesoporous organosilicas can be obtained by using various concentrations of divalent surfactant C_{16-3-1} or equimolar mixtures of divalent and monocationic surfactants as SDAs under basic conditions. Cubic $Pm\bar{3}n$ or 2D hexagonal $p6mm$ mesophases can be synthesized by changing the molar ratio of the binary surfactant mixtures or the amount of the base NaOH. Use of monocationic C_{16}TABr instead of C_{16-3-1} as template produced the hexagonal $p6mm$ mesophase exclusively independent of the amount of the surfactant and the base. In addition, use of trimethylbenzene as expander molecule in the aforementioned binary surfactant template system caused a mesophase transformation from cubic $Pm\bar{3}n$ to $p6mm$ symmetry. All samples were characterized by powder X-ray diffraction (PXRD) analysis and N_2 physisorption. The formation of face-centered cubic $Fm\bar{3}m$, primary cubic $Pm\bar{3}n$, and hexagonal $p6mm$ PMOs was also confirmed by transmission electron microscopy (TEM), revealing a good long-range ordering with regular arrays. Moreover, variation of the synthesis parameters resulted in a variety of different PMO morphologies, as ascertained by scanning electron microscopy (SEM). FT-IR and solid-state ^{13}C and ^{29}Si NMR spectroscopy further revealed that the organic groups were uniformly incorporated into the framework. The various BET surface areas of the PMOs range from 470 to 780 $\text{m}^2 \text{g}^{-1}$, while the pore diameters lie within a 26 to 30 Å range, as derived from N_2 physisorption.

Key words: Organosilicas, Cationic Surfactants, Mesoporous, Mesophase Transformation, Morphology