Ethylene-bridged Mesoporous Organosilicas with Hexagonal and Cubic Symmetry

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75\textsuperscript{th} 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\textsubscript{16}-3-1) or binary surfactant mixtures \([\text{CH}_3(\text{CH}_2)_{15}\text{NMe}_3]^+ \text{Br}^-\) (C\textsubscript{16}TABr) and C\textsubscript{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\textsubscript{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\textsubscript{16}TABr instead of C\textsubscript{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 \(\text{N}_2\) 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 \(^{13}\text{C}\) and \(^{29}\text{Si}\) 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 m\textsuperscript{2} g\textsuperscript{−1}, while the pore diameters lie within a 26 to 30 Å range, as derived from \(\text{N}_2\) physisorption.

\textit{Key words:} Organosilicas, Cationic Surfactants, Mesoporous, Mesophase Transformation, Morphology