

Ultra-fast hydrothermal synthesis of diastereoselective pure ethenylene-bridged periodic mesoporous organosilicas†

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A novel synthesis of diastereoselective pure periodic mesoporous ethenylene-silicas is presented, using (a) the homemade *E*-diastereoisomer of bis(triethoxysilyl)ethene, (b) a more efficient extraction procedure of the template P123 and (c) an ultra-fast synthesis procedure.

The development of ordered mesoporous silicas has recently been expanded by the introduction of hybrid materials with organic–inorganic frameworks.^{1,2} These multifunctional materials, called periodic mesoporous organosilicas (PMO's) are synthesized from bridged bisilanes (RO)₃Si–R'–Si(OR)₃ by means of the templating approach. They are a promising class of ordered mesoporous materials that combine the structural features of ordered mesoporous silicas with the chemical functionality of organic groups.^{1–5} From this perspective periodic mesoporous ethenylene-silicas are very interesting as they offer plenty of opportunities for further modification based on olefin chemistry.^{1,6,7}

PMO's are currently synthesized by mimicking synthesis conditions of mesoporous silica materials. However, we have established that these conditions are not ideal. In this contribution, we present (a) the easy synthesis of a diastereoselective pure bisilane; (b) an improved extraction method of the surfactant template and (c) a drastic reduction of the synthesis time.

Ethenylene-bridged PMO's are generally synthesized using bis(triethoxysilyl)ethene (BTSE) prepared according to a method described by Marciniak *et al.*⁸ This method results in a mixture of two isomers (~70% *E*).

By using the Grubbs' first-generation catalyst we were able to synthesize the pure *E*-diastereoisomer in a straightforward method. In a typical synthesis of BTSE, (PCy₃)₂Cl₂Ru=CHPh (0.0535 g, 0.065 mmol) and vinyltriethoxysilane (42.95 ml, 0.2038 mol) were added to a Schlenk flask under argon. The mixture was left to stir for one hour and subsequently refluxed for an additional hour. Unreacted vinyltriethoxysilane was distilled off, after which BTSE was vacuum distilled to give a clear colourless liquid (94% yield). The product was characterized with ¹H and ¹³C NMR and GC analysis (~100% *E*).

In our effort to obtain ethene-PMO's with high surface areas and large pore volumes, a fast, more efficient and mild extraction procedure for the surfactant template P123 was probed. PMO materials are commonly extracted with acidified ethanol,

regardless of the surfactant template employed. Acidified ethanol, the first extracting solvent for templated mesoporous materials, is a good solvent for the extraction of ammonium surfactants. Its efficiency however, for the removal of polymeric templates such as the triblock copolymer pluronic P123 has not been investigated yet in detail.

The extraction of pluronic P123 was examined and evaluated by means of FT-Raman spectroscopy. To exemplify the efficiency, the solvent extraction of P123 was initially studied for SBA-15. This inorganic material, with similar morphological and structural features as our PMO's has no active Raman vibrations, thus resulting in spectra with bands which can be assigned exclusively to the surfactant template. Fig. 1 shows the Raman spectra (C–H stretch region) of the as synthesized, solvent-extracted (5 h, soxhlet) and calcined SBA-15.

To assure reliable quantitative measurements a calibration curve was set up for P123, using CDCl₃ as an internal standard. In Table 1, the efficiency of several solvents for the extraction of P123 is given. From this table can be seen that acetone is the most efficient solvent removing over 94 mol% of the template after a single soxhlet extraction of 5 h.

The extraction of P123 was also studied for ethenylene-bridged PMO's, the results are given in Table 2. As can be seen from this table, the surface area, the total pore volume and the pore diameter increase due to the improved extraction procedure.

In our attempt to reduce the synthesis time, we found that the pH of the reaction mixture and the presence of additives play a key role. Lowering the pH increases both the silane-template interaction and the hydrolysis rate of the PMO-precursor.

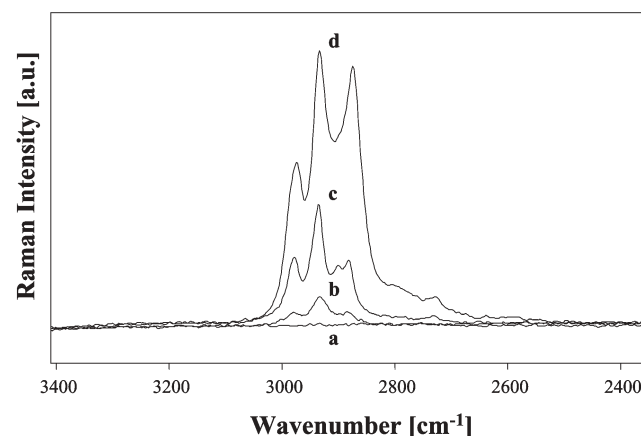


Fig. 1 Raman spectra of SBA-15: (a) calcined, (b) acetone-extracted (5 h), (c) ethanol-extracted (5 h), (d) as synthesized.

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Table 1 Extraction efficiency of several solvents for the removal of P123

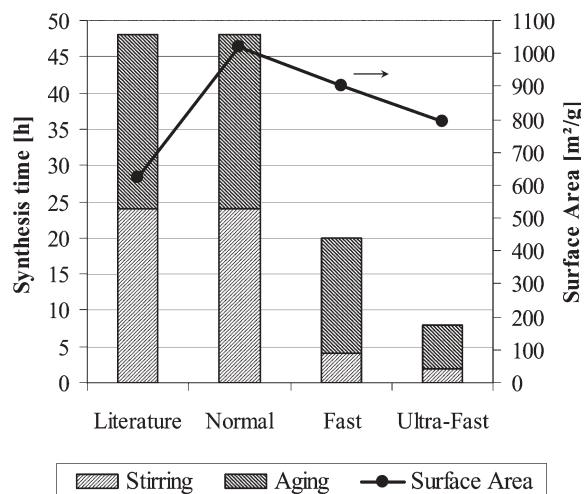
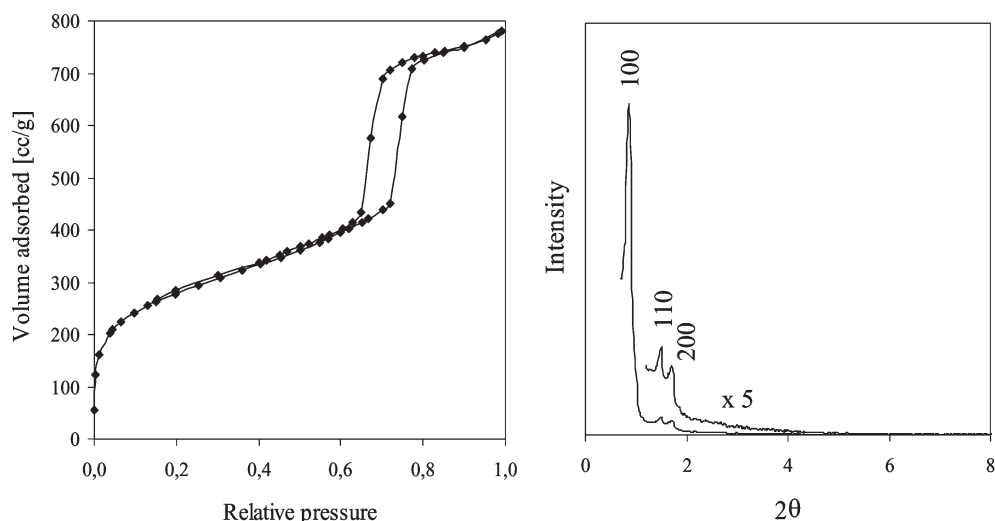
Extraction solvent	Mol% extracted ^a
Dichloromethane	66.7
Chloroform	69.9
Acidified ethanol	71.8
Ethyl acetate	77.0
Isopropanol	78.6
Acetone	94.2

^a Amount of P123 extracted after five hours.

Table 2 Structural properties of ethenylene-bridged PMO's

PMO samples	Surface area/m ² g ⁻¹	Total pore volume/cc g ⁻¹	Pore size ^a /nm
As synthesized	263	0.451	5.0
Ethanol-extracted	970	0.978	5.4
Acetone-extracted	1018	1.034	5.9

^a BJH pore diameter calculated from the desorption branch

**Fig. 2** Surface area as a function of the synthesis time.**Fig. 3** Nitrogen isotherms and powder X-ray diffraction pattern for a mesoporous ethenylene-bridged PMO.

However, this is only possible to a certain extent after which both the surface area and the pore volume start to drop due to the increasing kinetics of the sol-gel reaction. In order for the nanobuilding blocks to aggregate into a mesoporous architecture, a strong template-precursor interfacial energy and a minimal repulsion force between the growing organosilica particles is needed. Recent literature data indicate that additives such as salts and cosolvents can have dramatic effects on the morphology and structure of the obtained mesophases.^{6,9} Most intriguing was the effect of BuOH on the ordering of ethene-bridged PMO's published by Sayari *et al.*⁶

By combining the use of a diastereoselective pure precursor with an optimized synthesis route and an improved extraction method, we developed an ultra-fast hydrothermal synthesis procedure for ethenylene-bridged PMO's with outstanding structural properties.

In Fig. 2, the surface area is given as a function of the synthesis time. When compared to the literature,⁶ we were able to drastically reduce the synthesis time, whilst obtaining PMO's with higher surface areas. These materials also have large pore volumes and narrow pore size distributions. Furthermore, by developing the *E*-diastereoisomer of BTSE, we were able to synthesize a diastereoselective pure PMO. The diastereoselectivity of these PMO's was verified by FT-Raman spectroscopy. Fig. 3 shows the nitrogen isotherms and the powder X-ray diffraction pattern of an ethenylene-bridged PMO with 2D hexagonal symmetry, illustrating the high quality of the materials.

In a typical ultra-fast synthesis, 1.00 g of P123 was diluted in an acidified solution (pH of 0.5) containing 48.70 ml of H₂O, 2.12 ml of concentrated HCl and 1.17 ml of BuOH. The solution was stirred at room temperature for 1.5 h upon which 1.86 ml of the homemade pure *E*-diastereoisomer of bis(triethoxysilyl)ethene was added. This solution was stirred for 2 h at 35 °C and successively aged for an additional 6 h at 90 °C. The mixture was left to cool down to room temperature after which the precipitated PMO was filtrated and washed with distilled water. The surfactant was removed by means of soxhlet extraction using acetone over a period of 5 h.

In conclusion, an ultra-fast synthesis procedure for ethenylene-bridged PMO's with exceptional properties combined with an

improved extraction method for polymeric templates has been developed. Furthermore, using homemade diastereoselective pure bis(triethoxysilyl)ethene, the first diastereoselective ethene-PMO's have been synthesized.

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