Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information for:

Hybrid ceramic nanosieves: stabilizing nanopores with organic links

Hessel L. Castricum,* Ashima Sah, Robert Kreiter, Dave H.A. Blank, Jaap F. Vente and Johan E. ten Elshof

Inorganic Materials Science, MESA+ Institute for Nanotechnology, University of Twente, Postbus 217, 7500 AE, Enschede, The Netherlands. Fax: (+31) 53 4894683; Tel: (+31) 53 4892695; E-mail: castric@science.uva.nl

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

Energy Research Centre of the Netherlands, Postbus 1, 1755 ZG Petten, The Netherlands.

Experimental details

1. Materials

Distilled 1,2-bis(triethoxysilyl)ethane and methyltriethoxysilane (Aldrich) were mixed in equal molar amounts and added to dry ethanol. Distilled water and nitric acid were added dropwise under continuous stirring in an ice bath. After each water addition step, the sol was allowed to reflux at 60°C. The final ratios were [–OEt]:[H_2O] = 1 and [H^+]:[silane] = 0.1. Unsupported films were obtained by drying the sols in a Petri dish. The silica sol was coated onto a tubular alumina support system [1], which was prepared as follows. Macroporous α-alumina tubes (ID/OD=8/14 mm, length=1 m) were prepared by ceramic paste extrusion followed by sintering [2]. Two α-alumina layers were applied on the support tube by film-coating with α-alumina colloidal suspensions. On top of this, a boehmite sol was slip-coated, which, after drying and a heat treatment at 600°C, transformed into γ-alumina. Class 1000 cleanroom conditions were applied during the coating procedures to prevent defect formation by dust particles. All layers were applied on the outside of the support tube. The supported and unsupported materials were consolidated in N_2 (99.999% pure) at 300 °C for 3 h (0.5 K/min heating / cooling).

2. Sol characterisation

^{29}Si NMR was acquired on a Bruker 500 MHz NMR. Sol colloid sizes were determined by dynamic light scattering (DLS) at 22°C in a Malvern Zetasizer 3000HSa, and fractal dimensions by Small-Angle X-ray Scattering (range $1.26 < q < 2.5$ nm^{-1}). In Fig. S1, the colloid size, as determined with DLS is shown as a function of synthesis time (60 °C). A higher growth rate is observed after addition of water (after 90 minutes of refluxing). We used this dependency on the water content to tune the final sol colloid size.

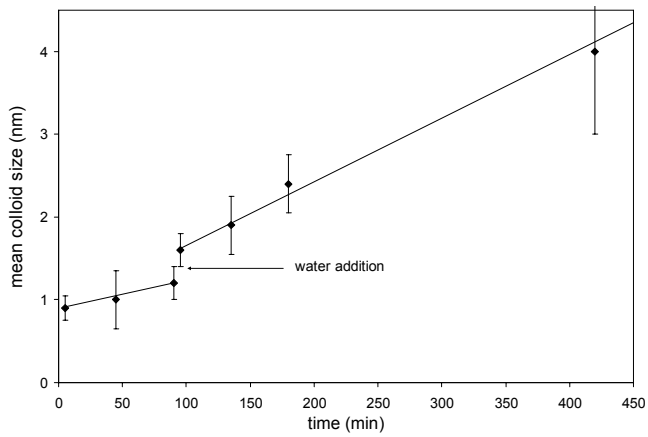

Fig. S1 Colloid size development with synthesis time. Addition of water after 90 minutes results in a higher growth rate.

3. Characterisation of supported and unsupported films

Sorption isotherms were obtained for consolidated unsupported films at 77 K (N_2) and 273 K (CO_2, C_2H_2) on a CE-Instruments Milestone 200. Surface areas were determined from the adsorption isotherms by the Dubinin method, modified by Kaganer [3], represented by:

$$\log n = \log n_m + D\,(\log p^0/p)^2$$

with n the gas adsorbed at relative pressure p/p^0, n_m the monolayer capacity of the surface, both in mol per g adsorbent, and D an adsorbate-dependent constant.
High-resolution Scanning Electron Microscopy was carried out on a LEO Gemini 1550 FEG-SEM at a voltage of 0.60 kV.

4. Membrane durability testing

Pervaporation was performed in an autoclave (150°C, 5 bar). Steady-state fluxes were determined by collecting the vapors at the permeate side of the membrane in a cold trap (10 mbar) and the composition assessed by Karl-Fischer titration.

[1] B. C. Bonekamp, in *Fundamentals of Inorganic Membrane Science and Technology*, (Ed: A. J. Burggraaf, and L. Cot), Elsevier, Amsterdam, The Netherlands 1996, p. 141.

[2] H. M. van Veen, Y. C. van Delft, C. W. R. Engelen and P. P. A. C. Pex, Sep. Purification Technol., 22-23, 2001, 361-366.

[3] S. J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, UK 1982; M. G. Kaganer, *Zh. Fiz. Khim.*, 1959, **33**, 2202.