Element–organic frameworks with high permanent porosity†

Marcus Rose,[a] Winfried Böhlmann,[b] Michal Sabo[a] and Stefan Kaskel*[a]

Received (in Cambridge, UK) 10th December 2007, Accepted 25th February 2008
First published as an Advance Article on the web 26th March 2008
DOI: 10.1039/b718925g

Microporous hydrophobic polysilanes with high specific surface areas (700–1100 m^2 g^{-1}) for applications in gas adsorption are obtained using an organolithiation route.

The search for novel porous materials with narrow pore size distribution, high accessible surface area and well defined functional groups on the inner surface is crucial for the development of applications in adsorption, separation, gas storage, and heterogeneous catalysis. A rational design was achieved in metal–organic frameworks (MOFs), coordination polymers consisting of connectors (metal ions or clusters) and linkers (organic molecules with functional groups) defining the network topology and pore diameter[1–4] and in covalent organic frameworks (COFs) as an extension of the modular concept using boronic acids as building blocks.[5,6] They surpass traditional molecular sieves such as zeolites and activated carbons in terms of surface area and specific pore volume. A disadvantage of these materials is the low hydrothermal stability in some cases.[7] Metals such as chromium in MIL-101 have a high toxicity.[8] Other porous organic–inorganic hybrid materials of great interest obtained in the last years are the periodic mesoporous organosilicas (PMOs)[9] and porous polymers.[10] Hypercrosslinked polymers (HCPs) were obtained by hypercrosslinking of polymer chains in a swollen polymer to generate a rigid, porous polymer network.[11–13] Another approach is the polymerization of large rigid molecules to form chains and networks with inefficient space packing and voids in the range of micropores, realized in the polymers of intrinsic microporosity (PIMs).[14,15] Recently Cooper *et al.* published the synthesis of conjugated microporous polymers (CMPs) using Sonogashira–Hagihara coupling of alkynes with aryl halogens.[16] They showed that the pore size of the obtained amorphous microporous polymers depends on the size of the organic linker.

Our interest was to develop a new class of microporous materials ($d < 2$ nm) with high hydrophobicity, high stability against water and good thermal stability using the modular concept of connectors and linkers but an organometallic polymer synthesis route. In the following, we report the integration of elements such as silicon and their use as connectors. At the same time, organic linkers are used to tailor the pore size, resulting in a porous, highly hydrophobic and thermally stable element organic framework (EOF).

Tetrakis(4-bromophenyl)silane (TBPS), was used as the primary building block. The synthesis of TBPS was reported earlier by Fournier *et al.*[17] TBPS was lithiated fourfold by reaction with *n*-butyllithium under inert conditions. Subsequent reaction with tetraethylorthosilicate (TEOS) at 263 K resulted in the formation of the porous network poly(1,4-phenylene)silane (EOF-1, Scheme 1). The white product is separated from the solution by centrifugation. EOF-1 forms as an X-ray amorphous precipitate composed of very small particles. Instead of TEOS, $SiCl_4$ can be used for the framework formation but the specific surface area is slightly reduced. A biphenylene linker was used to obtain larger pores in poly(4,4′-biphenylene)silane (EOF-2). Since 4,4′-dibromobiphenylene can be lithiated twofold, EOF-2 can be synthesized in a one-step reaction (Scheme 1), thus the synthesis of the tetrahedral precursor tetrakis(4-bromobiphenylene)silane is unnecessary.

The particle size and the morphology of the resulting particles was characterized by SEM analysis (Fig. 1). EOF-1 consists of spherical particles with a diameter of 0.1–0.5 μm while EOF-2 forms a dendritic network of flat particles.

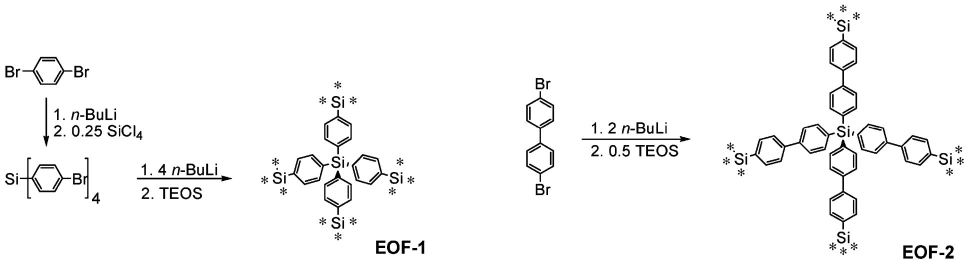
Both polymers are X-ray amorphous. The *para*-substituted phenylene group (EOF-1) is detected in the ^{13}C CP MAS NMR spectrum (δ = 131.7, 124.1 ppm). A shoulder at 139.5 ppm indicates the presence of non-symmetric substituted linkers due to incomplete conversion of Ph–Br groups. In the ^{29}Si MAS NMR spectrum one sharp peak at −17.9 ppm reflects the majority of $SiPh_4$-groups but a broader region at −33 to −43 ppm indicates the presence of some aliphatic substitution of Si atoms (see supporting information). EOF-1 and EOF-2 have a good thermal stability in air up to 673 K. A complete degradation is only observed above 873 K. They show no decomposition by air, moisture, or aqueous solutions.

Both compounds are highly porous. From the nitrogen physisorption isotherms measured at 77 K (Fig. 2), the specific surface areas determined using the BET equation are 780 m^2 g^{-1} (EOF-1) and 1046 m^2 g^{-1} (EOF-2). Using the t-plot method, a specific micropore volume is determined for EOF-1 with 0.32 cm^3 g^{-1} and for EOF-2 with 0.45 cm^3 g^{-1}. The external specific surface area is high for both compounds (167 m^2 g^{-1} (EOF-1) and 201 m^2 g^{-1} (EOF-2)).

---

[a] *Department of Inorganic Chemistry, Dresden University of Technology, Mommsenstr. 6, D-01069 Dresden, Germany. E-mail: stefan.kaskel@chemie.tu-dresden.de; Fax: +49-351-46337287; Tel: +49-351-46334885*
[b] *Faculty of Physics and Earth Science, University of Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany. E-mail: bohlmann@physik.uni-leipzig.de; Fax: +43-341-9732769; Tel: +49-341-9732613*

† Electronic supplementary information (ESI) available: Experimental procedures, NMR, IR and Raman spectra, DTA/TG diagrams and H_2 and CH_4 physisorption isotherms for EOF-1 and EOF-2. See DOI: 10.1039/b718925g



Scheme 1 Synthesis of EOF-1 and EOF-2.

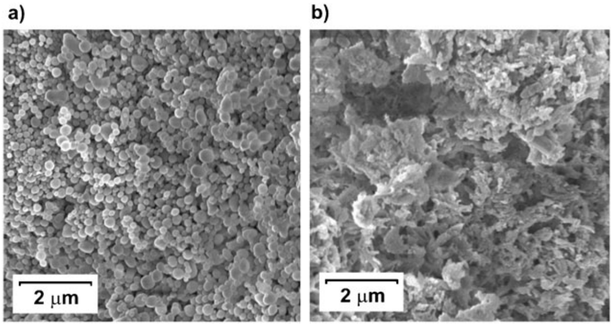


Fig. 1 SEM analysis of EOF-1 (a) and EOF-2 (b).

The isotherms are a combination of type I and II according to IUPAC.[18] The high uptake at very low pressures indicates a high microporosity. With increasing pressure, the nitrogen uptake increases, too. This indicates a high external surface area due to the presence of very small particles. The increasing uptake at high relative pressure ($p/p_0 > 0.9$) could be attributed to the presence of macropores or interparticular space. Both isotherms show a hysteresis extending to low relative pressure. This phenomenon was already mentioned by McKeown *et al.* in their work on PIMs (polymers of intrinsic microporosity).[14,15] Similar effects were interpreted earlier (a) as an effect of activated adsorption, (b) as a result of swelling in a flexible polymer framework, or (c) as a restricted access of nitrogen molecules to pores blocked by narrow openings.[11,14] For amorphous polymers such as in EOF-1 and 2, a swelling (b) is reasonable. A further hint in this direction is the high loss of volume of the samples, when they are dried after synthesis.

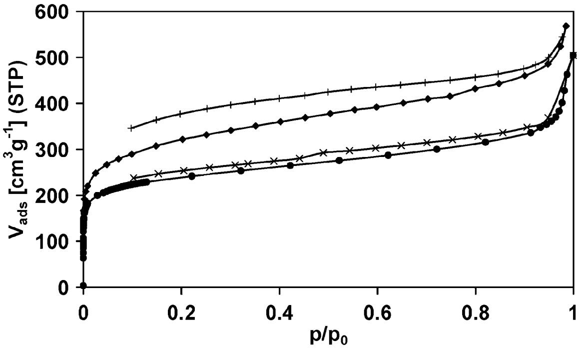


Fig. 2 N_2 adsorption and desorption isotherms at 77 K for EOF-1 (ads ●, des ×) and EOF-2 (ads ◆, des +) show hystereses over the whole range of relative pressure.

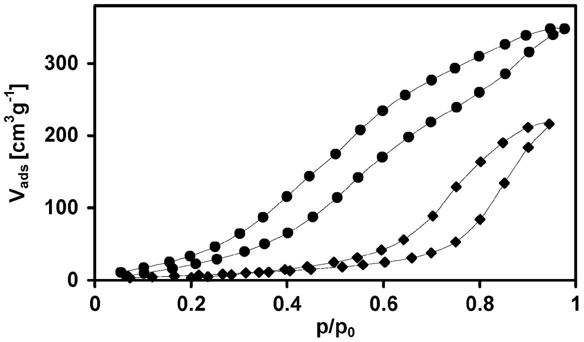


Fig. 3 Water vapor physisorption isotherms for EOF-1 (●) and EOF-2 (◆) measured at 298 K.

The hydrogen physisorption isotherms of both compounds were measured at 77 K. EOF-1 and EOF-2 adsorb 0.94 and 1.21 wt% hydrogen at a pressure of 1 bar. These values show that the EOFs have a hydrogen storage capacity comparable to PIMs and HCPs[19] and that they are promising materials for hydrogen storage, too.

The Gibbs excess adsorption of methane was measured at 303 K. EOF-1 shows a maximum excess adsorption at 50 bar (4.8 wt%). The maximum storage capacity of EOF-2 is 6.2 wt% at 85 bar. The isotherm of compound EOF-2 shows a hysteresis like the nitrogen physisorption isotherms indicating a swelling effect of the material, too.

Water adsorption isotherms at 298 K show a high hydrophobicity for both materials (Fig. 3). Especially EOF-2 is comparable with commercial activated carbons, because a significant adsorption of water vapor takes place at a relative pressure higher than 0.6.[20]

The combination of a high porosity and hydrophobicity of the compounds is very promising for applications in the adsorption of non-polar gases, which is necessary for example in air purification, or removal, or for the extraction of organic molecules from aqueous solutions. As compared to activated carbons being used in such applications, the EOF concept allows the integration of well defined organic linkers with predefined functionality. An advantage in comparison with MOFs and zeolites is the low uptake of water from the air in ambient conditions. Thus, a high capacity for the adsorption of hydrophobic gases is retained even without activation in a vacuum.

Summarizing, we have presented a new approach for the design of hydrophobic microporous frameworks with accessible pore system for nitrogen, hydrogen, and methane using organo-element chemistry. In our view, an extension of the concept in terms of elements used as nodes and organic linkers as connectors will lead to valuable adsorbents and catalyst supports with well defined porosity and functionality.

Notes and references

1 S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
2 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.
3 S. Kaskel, in *Handbook of Porous Solids*, ed. F. Schüth, K. S. W. Sing and J. Weitkamp, Wiley-VCH, Weinheim, 2002.
4 G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217–225.
5 A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.
6 H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Cote, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268–272.
7 M. Sabo, A. Henschel, H. Fröde, E. Klemm and S. Kaskel, *J. Mater. Chem.*, 2007, **17**, 3827–3832.
8 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
9 F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216–3251.
10 C. Weder, *Angew. Chem.*, 2008, **120**, 456–458.
11 M. P. Tsyurupa and V. A. Davankov, *React. Funct. Polym.*, 2006, **66**, 768–779.
12 C. D. Wood, B. Tan, A. Trewin, H. Niu, D. Bradshaw, M. J. Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stöckel and A. I. Cooper, *Chem. Mater.*, 2007, **19**, 2034–2048.
13 J. Germain, J. M. J. Fréchet and F. Svec, *J. Mater. Chem.*, 2007, **17**, 4989–4997.
14 B. S. Ghanem, K. J. Msayib, N. B. McKeown, K. D. M. Harris, Z. Pan, P. M. Budd, A. Butler, J. Selbie, D. Book and A. Walton, *Chem. Commun.*, 2007, 67–69.
15 N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675–683.
16 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2007, **46**, 8574–8578.
17 J.-H. Fournier, X. Wang and J. D. Wuest, *Can. J. Chem.*, 2003, **81**, 376–380.
18 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603–619.
19 N. B. McKeown, P. M. Budd and D. Book, *Macromol. Rapid Commun.*, 2007, **28**, 995–1002.
20 J. Pires, M. L. Pinto, A. Carvalho and M. B. de Carvalho, *Adsorption*, 2003, **9**, 303–309.