Mendeleev Commun., 2001, 11(6), 208–210

Polyfunctionalised surfactant-templated adsorbents with high specific surface areas

**Yurii L. Zub,*[a] Inna V. Seredyuk,[a] Alexei A. Chuiko,[a] Mietek Jaroniec,[b] Merfyn O. Jones,[c]
Richard V. Parish[c] and Stephen Mann*[d]**

[a] *Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 03164 Kiev, Ukraine. E-mail: zub@ukma.kiev.ua*
[b] *Department of Chemistry, Kent State University, Kent, Ohio 44242, USA*
[c] *Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, UK*
[d] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK. E-mail: S.Mann@bristol.ac.uk*

10.1070/MC2001v011n06ABEH001486

The single-step synthesis and structure–adsorption characteristics of trifunctionalised surfactant-templated adsorbents are described.

Designing adsorption selectivity is of importance in the development of materials for advanced catalytic, environmental and nanotechnological applications. It is possible to distinguish between structural (geometrical) selectivity arising from the presence of pores of certain shape and size and chemical selectivity arising from the presence of functional groups on the surface of the adsorbent. Thus, modern adsorption applications require materials with both tailored structural and surface properties. A simple and effective method for the synthesis of such adsorbents in one step involves the use of two or more functional components and a suitably matched templating agent. For example, functional trialkoxysilanes $(RO)_3SiR'$ can be used as a source of desired functional groups R′, tetraalkoxysilanes $Si(OR)_4$, as a framework-building agent, and surfactant micelles, as a mesostructure-directing template. This template-directed co-condensation approach is very promising because of the availability of various $(RO)_3SiR'$ organosilanes and self-assembled organic aggregates.[1]

It was found previously that two-component mixtures of alkoxysilanes can be used for preparing surfactant-templated mesoporous adsorbents with high surface areas and functional groups such as aryl,[2] amine,[3,4] thiol[4–6] and sulfate groups.[7,8] To the best of our knowledge there is only one report describing a bifunctionalised MCM-type silica prepared from a mixture of tetraethoxysilane (TEOS) and two different organo-functionalised silanes.[9] Here, we report the one-stage synthesis and structure–adsorption characteristics of surfactant-templated adsorbents prepared using four-component mixtures of organosilanes. This approach allows us to tailor not only the porous structure of the resulting adsorbents but also their surface functionality by introducing up to three types of covalently linked organic groups.

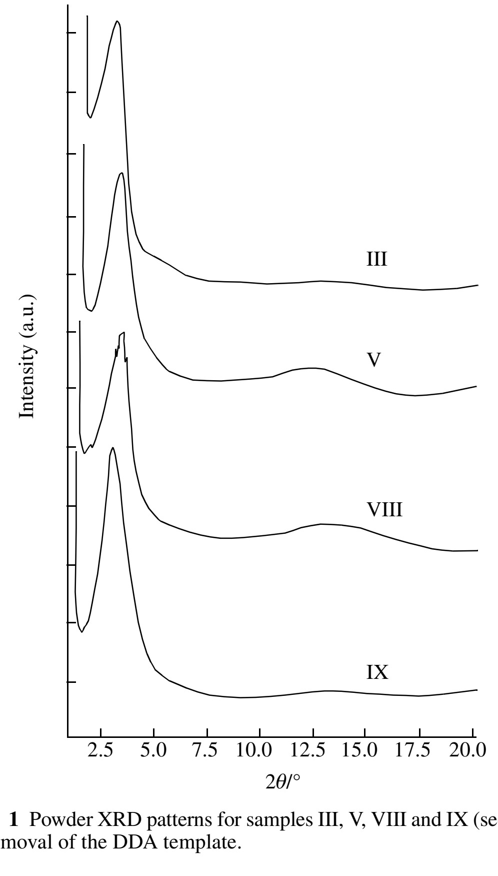

Figure 1 Powder XRD patterns for samples III, V, VIII and IX (see Table 1) after removal of the DDA template.

Trifunctionalised organosilica–surfactant mesophases were synthesised at room temperature and ambient pressure using mixtures of varying molar ratios of TEOS and functional organotrialkoxysilanes (FOS) in the presence of the neutral surfactant *n*-dodecylamine (DDA). Various combinations were studied (Table 1). The molar composition of a typical reaction mixture was 0.1 TEOS : 0.02 (total) FOS : 0.03 DDA : (2.2–2.8) H_2O.[†] The following FOS were used: 3-aminopropyltriethoxysilane (APTES), 3-mercaptopropyltrimethoxysilane (MPTMS), *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPED), bis[3-(trimethoxysilyl)propyl]amine (BTMPA), methyltrimethoxysilane (MTMS) and phenyltriethoxysilane (PTES). In each case, the surfactant was removed by solvent extraction to produce polyfunctionalised porous silicas.

Low-angle powder X-ray diffraction (XRD) data[‡] indicated that a single phase was formed in materials containing up to 20 mol% FOS in the initial synthesis mixture. In each case, a single peak was observed, indicative wormlike mesostructures[10] (Figure 1). Except for materials prepared from mixtures of TEOS/APTES/MPTMS or TEOS/TMPED/MPTMS, the functionalised mesostructures remained intact after surfactant extraction, although small lattice contractions were sometimes observed (Table 1). The XRD data were confirmed by transmission electron microscopy (TEM) images,[‡] which showed no evidence for a long-range ordered mesostructure after surfactant removal. Scanning electron microscopy studies of the polyfunctionalised adsorbents indicated that spherical particles were formed in each sample.[‡]

[†] *Typical conditions*: continuous stirring, 22.30 cm^3 (0.1 mol) of TEOS, 1.56 cm^3 (0.0067 mol) of APTES, 1.26 cm^3 (0.0067 mol) of MPTMS, and 0.95 cm^3 (0.0067 mol) of MTMS were added to 5.56 g (0.03 mol) of DDA in 60 cm^3 of absolute EtOH. Then, without termination of stirring, 40 to 50 cm^3 of water was added drop-by-drop for 2 min (up to the appearance of turbidity). After 1 min, a substantial amount of a white precipitate was formed. The precipitate was allowed to stand for 24 h at room temperature, then filtered off, quickly washed with 50 ml of EtOH and dried in air for 24–48 h. Extraction of the template was carried out in boiling MeOH for 3 h (3×300 ml of MeOH per 10 g sample). The white precipitate was dried *in vacuo* for 4 h.

[‡] X-Ray diffraction powder patterns were collected on a Scintag XDS2000 diffractometer using Copper radiation having a wavelength of 1.54060 Å. TEM images were recorded on a JEOL JEM-2000 FXII electron microscope operated at 300 kV. Samples were dispersed ultrasonically in EtOH, and a drop of the suspension was air-dried onto a carbon-coated grid. Scanning electron micrographs (SEM) were obtained with a JEOL Superprobe 733 microscope. Infrared spectra were recorded on a Nicolet 5 PC FT spectrophotometer using samples pressed with KBr. High-resolution solid-state ^{13}C CPMAS and ^{29}Si DPMAS NMR measurements were carried out on a Varian UNITYplus spectrometer and 7 mm (rotor o.d.) Doty Scientific MAS probe (with respect to an external reference sample of tetramethylsilane). Thermal analysis was performed in the range 20–800 °C with a heating rate of 5 °C min^{-1} (in an air stream; E. Paulik, J. Paulik, L. Erdey System, Q-1500 D).

Table 1 Characterization of the polyfunctionalised surfactant-templated materials.

Composition	XRD *d* spacing/Å (AS/SE)^a	Nitrogen adsorption			Amino content/ mmol g^{-1}	SH content/ mmol g^{-1}	Carbon^d content/ mmol g^{-1}
		BET surface area^b/m^2 g^{-1}	V_s/cm^3 g^{-1}	Pore size,^{c} *d*/nm			
I. TEOS/APTES/MPTMS	32.4/—	74	0.04	1.7	1.16	0.97	1.53
II. TEOS/TMPED/MPTMS	30.8/—	76	0.14	2.8	2.20	0.97	2.17
III. TEOS/BTMPA/MPTMS	37.5/37.4	725	0.48	3.0	0.79	0.44	3.45
IV. TEOS/APTES/MPTMS/MTMS	31.9/31.2	490	0.24	2.1	0.80	0.70	2.45
V. TEOS/APTES/MPTMS/PTES	31.6/31.6	490	0.24	1.8	0.65	0.67	5.87
VI. TEOS/TMPED/MPTMS/MTMS	33.2/32.2	450	0.32	2.1	1.46	0.71	2.66
VII. TEOS/TMPED/MPTMS/PTES	30.0/29.6	390	0.19	1.8	1.55	0.70	7.05
VIII. TEOS/BTMPA/MPTMS/MTMS	32.4/31.9	825	0.37	2.3	0.65	0.54	3.99
IX. TEOS/BTMPA/MPTMS/PTES	31.7/31.9	720	0.34	2.2	0.58	0.57	6.71

^{a}AS = as synthesised, SE = surfactant extracted. ^{b}Relative pressures from 0.05 to 0.20 were used. ^{c}Calculated at the maximum of pore size distribution using the KJS method.[11] ^{d}Carbons of amino and mercaptopropyl groups (calculated from %N and %S) are not included.

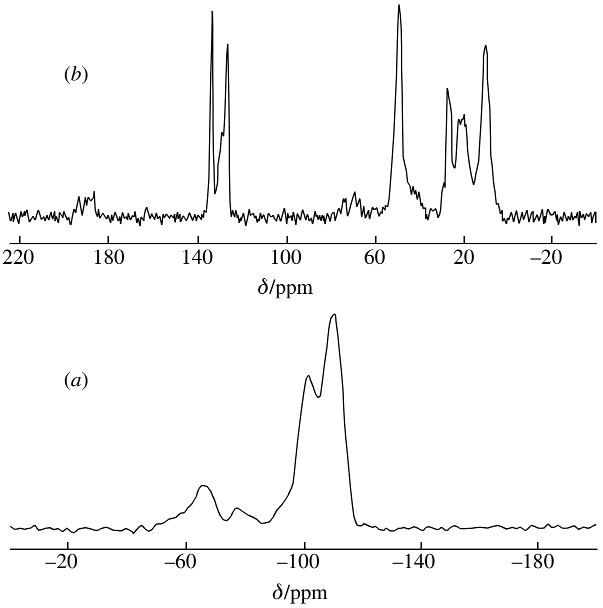

Figure 2 (*a*) ^{29}Si DPMAS NMR spectrum and (*b*) ^{13}C CPMAS NMR spectrum of sample IX after surfactant extraction.

Nitrogen adsorption studies (Table 1) confirmed that the surfactant-extracted materials possessed pores ranged in size between micro- and mesoporosity. The pore size at the distribution maximum, calculated using the KJS method,[11] were between 1.8 and 3 nm. In general, a decrease in the pore size was observed when PTES was used as one of the components, whereas higher specific surface areas were obtained in the presence of BTMPA. The presence of arched structures consisting of [$O_3Si(CH_2)_3$–NH–$(CH_2)_3SiO_3$] linkages on the pore surface could be responsible for the larger pore diameters.

The IR spectra‡ exhibited a strong absorption band in the range between 1060 and 1195 cm^{-1} characteristic of functionalised polysiloxanes. The band was split into two components (or a shoulder), consistent with the formation of a three-dimensional skeleton.[12] The IR spectra also showed bands characteristic of R′ functional groups. The samples heated to 150 °C *in vacuo* exhibited three or sometimes four resolved weak $\nu_{s,as}$ (CH) bands indicating the presence of thermally stable methoxy (≡Si–OMe) groups on the surface,[13] which are formed during the methanol extraction of the template. This is supported by the following observations: first, an excess in the carbon content (Table 1); second, the IR spectrum of the silica sample obtained from TEOS in the presence of DDA using the same experimental procedure exhibited three bands at 2856, 2930 and 2965 cm^{-1}, which remained after heating the sample *in vacuo* at 200 °C, whereas the IR spectrum of this sample calcined at 540 °C in order to remove DDA does not show these bands; third, the ^{13}C CPMAS NMR spectrum of the extracted sample showed a signal at 49.0 ppm, which is typical of MeOSi≡, and this signal was present after heating the sample *in vacuo* to 105 °C.

The incorporation of covalently linked organic groups was also confirmed by ^{29}Si DPMAS NMR spectroscopy,‡ which revealed well-defined resonances for siloxane [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4] and organosiloxane [$T^m = R'Si(OSi)_m(OH)_{3-m}$, $m = 2$–3] environments. For instance, in the case of sample IX, which contains aminopropyl, mercaptopropyl and phenyl moieties, the ^{29}Si DPMAS spectrum showed two major sets of resonances from –90 to –110 and at *ca.* –70 ppm, respectively [Figure 2(*a*)]. The first region contains two intense peaks at –110.2 and –101.4 ppm and one very weak peak at –92.7 ppm, which were assigned to Q^4, Q^3 and Q^2, respectively. The distinct peak at –66.5 ppm was assigned to T^3(propyl), the shoulder at –58.8 ppm to T^2(propyl), and the weak peak at –77.0 ppm and the shoulder at –80.7 ppm, to the T^2 and T^3 units, respectively, containing covalently linked phenyl groups. The trifunctional nature of the materials was also corroborated by ^{13}C CP MAS NMR studies. For sample IX, for example, signals attributed to propyl chains linked to silicon atoms (δ is 10.4, 20.4, 27.4 and 49.7 ppm) and phenyl carbons (127–134 ppm) were observed [Figure 2(*b*)].

The thermal analysis‡ of samples III, VIII and IX indicated the loss of residual solvent with maxima at 80, 100 and 130 °C, respectively. This was followed by minor mass losses (*ca.* 4.2, 2.8 and 3.5%) centered at 340, 350 and 320 °C, and major losses (*ca.* 13.6, 12.5 and 16.5%) centered at 583, 572 and 590 °C, respectively. These data indicate that the polyfunctionalised materials were stable with covalently bonded organic groups.

The above results indicate that the surfactant-directed co-condensation of TEOS and organosilanes can be extended to a combination of three organic functionalities that are covalently linked to the porous silica framework. Such materials should be useful in a wide range of applications such as the adsorption of toxic metal ions[1] and catalysis.[14] It should be possible to extend the synthesis strategy to polyfunctionalised silica-based adsorbents in the form of thin films and monoliths. The preparation of hybrid nanoporous and mesoporous siliceous materials with controlled multi-functionality, porosity and hydrophobicity could also open up new avenues for research in metalloorganic, organic and inorganic host–guest chemistry.

Yu. L. Z. thanks The Royal Society for a partial financial support of this work. The NSF grant CTS-0086512 (M.J.) is gratefully acknowledged. We thank Dr. D. C. Apperley (University of Durham) for the solid state NMR data and Dr. H. Honda (Tsukuba Research Laboratory, Sumitomo Chemical Co., Ltd) for TEM figures.

References

1 J. Brown, L. Mercier and T. J. Pinnavaia, *Chem. Commun.*, 1999, 69.
2 S. L. Burkett, S. D. Sims and S. Mann, *Chem. Commun.*, 1996, 1367.
3 D. J. MacQuarrie, *Chem. Commun.*, 1996, 1961.
4 C. E. Fowler, S. L. Burkett and S. Mann, *Chem. Commun.*, 1997, 1769.
5 R. Richer and L. Mercier, *Chem. Commun.*, 1998, 1775.
6 Y. Guo and A. R. Guadalupe, *Chem. Commun.*, 1999, 315.
7 W. M. Van Rhijn, D. E. De Vos, B. F. Sels, W. D. Bossaert and P. A. Jacobs, *Chem. Commun.*, 1998, 317.
8 M. H. Lim, C. T. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467.

9 S. R. Hall, C. E. Fowler, B. Lebeau and S. Mann, *Chem. Commun.*, 1999, 201.
10 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
11 M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 1997, **13**, 6267.
12 L. P. Finn and I. B. Slinyakova, *Kolloidn. Zh.*, 1975, **37**, 723 [*Colloid J. USSR* (*Engl. Transl.*), 1975, **37**, 651].
13 Wei Li and R. J. Willey, *J. Non-Cryst. Solids*, 1997, **212**, 243.
14 D. J. MacQuarrie and D. B. Jackson, *Chem. Commun.*, 1997, 1781.

Received: 18th June 2001; Com. 01/1812