Novel super-microporous silicate templating by ω-hydroxyalkylammonium halide bolaform surfactants

Stephen A. Bagshaw[*a] and **Alan R. Hayman**[b]

[a] *Advanced Materials Group, Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand.
E-mail: s.bagshaw@irl.cri.nz*
[b] *Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand.
E-mail: hayman@alkali.otago.ac.nz*

Templated silicate molecular sieves exhibiting templated super-micropores in the range 1.0–2.0 nm and interesting pore symmetries bearing similarity to the Lα, SBA-2 ($P6_3/mmc$) and Mα (cmm) phases have been prepared by exploiting the novel aggregation properties of a new family of ω-hydroxyalkylammonium bolaform surfactants.

Recently, a series of papers have described the formation of mesostructured silicates[1–3] and microporous transition metals oxides by exploiting the aggregation properties of bifunctional 'bolaform' surfactants.[4–8] These new templating systems have produced pillared-lamellar and M41S type mesostructures and most recently, an intermediate phase possessing the *cmm* space group. Unlike earlier work which focused on known surfactant systems,[1] Stucky and coworkers[6] exploited new design in surfactant molecular structure. Indeed mesostructures have been prepared that do not mimic any known surfactant liquid crystal phases.[6,9]

One of the synthetic goals identified early in the development of this field was the formation of materials possessing regular pores in the range 1.2–2.0 nm, that would allow shape selective catalysis of organic molecules too large to be accessed by zeolites. It is clear that while normal M41S materials exhibit great promise in the processing of long-chain and bulky hydrocarbons, they do not possess desirable shape selectivity.[2] The elegant preparation of extra-large pore crystalline alumino-silicate zeolite compositions such as UTD-1,[10] the PCH materials,[11] recent efforts at post-synthesis pore-mouth modification of MCM-41[12] and the ubiquitous pillared-clays[13] are among the somewhat few successful efforts at accessing the super-microporous region.

Here, we report preliminary results of the exploitation of a new family of ω-hydroxy-bolaform surfactants.[14,15] These surfactants have permitted the *a priori* design of templated super-microporous silicate structures. Primarily, the ω-hydroxy-bolaform surfactants form micelles in aqueous solution with low aggregation numbers and diameters approximately half those of the parent alkylammonium halide surfactants.[15] Secondly, it is implicit from the geometry of the aggregates that the polar ω-hydroxy groups be located near the micelle surface. Thus, the hydroxy group could conceivably be involved in additional H-bonding at the organic/water/inorganic interface thus modifying the effective surfactant headgroup area and thus the micelle packing and subsequent pore symmetries.

The bolaform surfactants $HO(CH_2)_{16}NR_3^+Br^-$ (R = Me or Et), were evaluated as potential templates. The materials we describe herein were prepared by substituting the new templates directly into existing M41S synthesis methods[16] from the following gel compositions: $4.0\ SiO_2$: $x\ HO(CH_2)_{16}NEt_3^+Br^-$: $3.0\ NaCl$: $2.0\ NaOH$: $0.34\ NH_3 \cdot H_2O$: $236\ H_2O$ (x = 0.40, 0.55, 0.70, 0.85). The high Krafft temperature, 63 °C,[16] of the trimethylammonium derivative precluded its use owing to poor solubility during the preliminary stages of the reaction. The triethyl surfactant has a much lower Krafft temperature, around room temperature, and hence an acceptable solubility.

Powder X-ray diffraction (XRD) patterns of selected samples prepared with different Si : surfactant ratios are presented in Fig. 1. The pattern in Fig. 1 of the as-prepared sample **A** (see Table 1), appears to describe a lamellar (Lα) phase, exhibiting strong d_{100} and weak d_{200} reflections. This material does not completely collapse upon calcination which suggests that a porous structure not based on a layered motif has been retained. The calcined material **B** (Fig. 1) produces a multireflection pattern that may possibly be indexed to a 3-D cubic ($P6_3/mmc$) array.[7] The XRD pattern of the calcined sample **C** (Fig. 1) is very similar to that described for the hexagonal Mα (cmm) liquid crystal phase.[18] The major Bragg reflections from all the materials formed were found at higher angles than those reported for M41S or SBA-8 type materials.[1,6] This is the first evidence that the repeat units formed are smaller than those of 'typical' mesostructured materials.

The formation of super-micropores was further supported by N_2 sorption isotherms (Fig. 2). Neither the Langmuir nor the
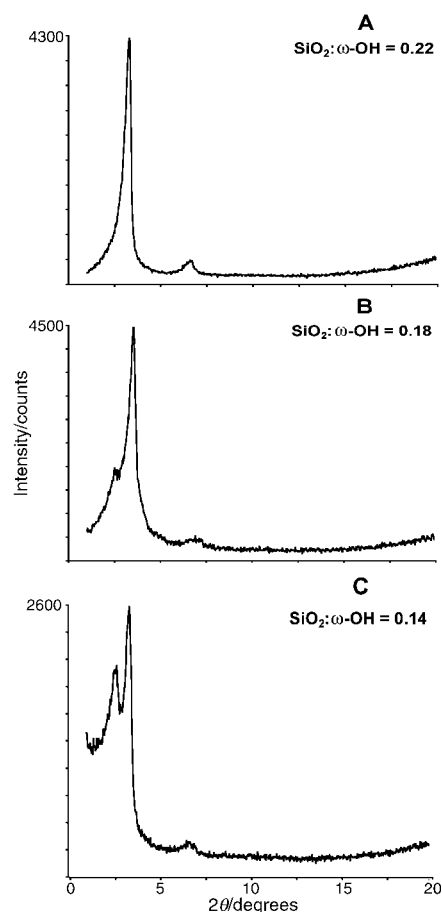

Fig. 1 XRD patterns of $HO(CH_2)_{16}NEt_3^+Br^-$ templated super-microporous silicas with different Si : surfactant ratios as indicated.

Table 1 Physico-chemical characteristics of super-microporous silica samples

Sample	$SiO_2 : \omega$-OH	$d_{hk0}{}^a$/nm	Pore diameter^b/nm		Surface area^c/ m^2 g^{-1}	Pore volume^d/ mL g^{-1}
			BJH	HK		
A	1.0:0.22	4.7, 2.3	1.4	1.5	950	0.50
B	1.0:0.18	4.0, 2.9	1.6	2.1	1130	0.75
C	1.0:0.14	4.0, 3.1	1.6	2.1	870	0.65
D	1.0:0.10	n.o.^{e}	1.4	1.4	550	0.75
E^f	1.0:0.2	3.3	1.5	1.4	505	0.70

^{a} ±0.1 nm; values taken from most intense XRD reflections. ^{b} ±0.1 nm. ^{c} ±10 m^2 g^{-1}; surface areas calculated using the BET model. ^{d} ±0.05 mL g^{-1}; pore volumes calculated from p/p_0 = 0.98. ^{e} n.o. = Not observed. ^{f} Al incorporated at 2.0 mol% with respect to Si.
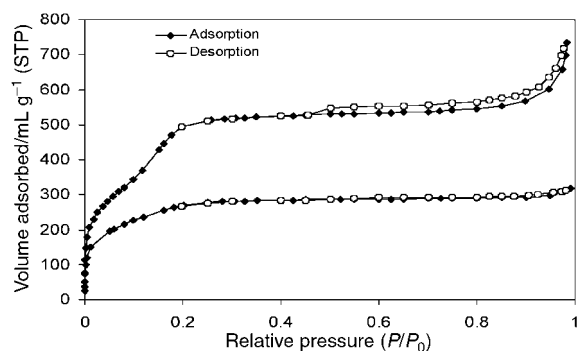

Fig. 2 Nitrogen adsorption–desorption isotherms of calcined samples corresponding to samples **B** (upper) and **E** (lower) in Table 1. Isotherm **B** has been offset along the Y axis for clarity.

BET model plots from the isotherms of these materials were linear thereby suggesting incompatabilities of the models with pores in this size regime. The BET model however, remains the most accessible and has thus been used here for indicative surface area determination. Surface areas and pore volumes (Table 1) of a selection of the materials prepared are relatively high, indicating that the pore structures of the new materials are well ordered and accessible. The isotherms of the most well defined materials *e.g.* **B** in Fig. 2 are typical reversible type IV curves[19] with small hysteresis of the desorption branch. The most interesting feature is the clear capillary condensation step at very low relative pressure (P/P_0 = 0.15). This is lower than any previously reported templated mesostructured material. The presence of an adsorption upturn at high partial pressures is suggestive of textural or indeed other non-specific meso-porosity. Pore diameters as calculated by the BJH method[19] centre around 1.6 nm, while HK calculations[19] centre around 2.0 nm (Table 1). However, the reliability of these common methods for pore size determination when applied to templated mesostructured materials has recently been questioned.[20]

Particle morphologies as determined by scanning electron micrographs (SEM) show particles of *ca.* 100 µm diameter that appear to be agglomerations of primary particles. Transmission electron micrographs (TEM) of micro-sectioned samples (Fig. 3) confirm the existence of pores of below 2.0 nm diameter. The TEM images are ambiguous with respect to the rigorous determination of pore symmetry and diameter, but do suggest the presence of hexagonal or similar symmetry among a generally disordered pore system. TEM data also indicated that the particles were not 'solid' but have highly open internal structures. This would explain the upturn in adsorption at higher nitrogen relative pressures. The reason for the formation of these particle morphologies however, is not known at this time.

We have been moderately successful, at this stage, in forming Al and Ti substituted materials with the goal of introducing catalytic function. As is often observed in M41S syntheses, the Al substituted materials were less ordered than the pure silica analogues and possessed smaller pore diameters as is evidenced in the type I nitrogen isotherm (sample **E**, Table 1, Fig. 2). The
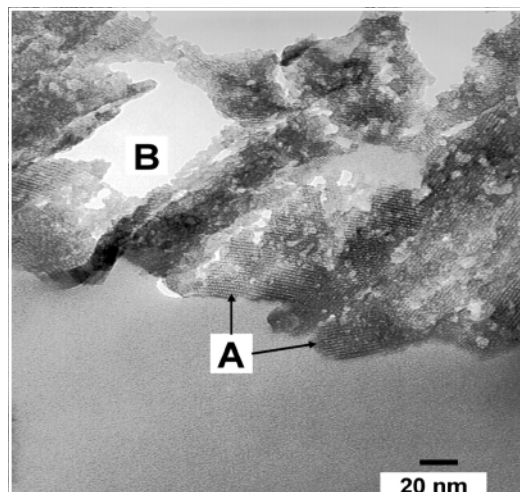

Fig. 3 Transmission electron micrograph of calcined sample **B** showing (*a*) ordered super-micropores and (*b*) open structure of the particles.

preparation of further novel super-microporous compositions from $HO(CH_2)_nNR_3{}^+Br^-$ surfactants where n = 12 or 14 and R = propyl and pyridyl is also continuing. It is anticipated that the reduction in the length of the alkyl chain of the surfactant from C_{16} will further reduce the pore diameters into the 1.2–1.5 nm region, although the increased solubility of these shorter surfactants may introduce new synthetic challenges. Indeed, early results indicate that ω-$HO(CH_2)_{12}NEt_3Br$ templated silicates do have pores in the range 1.0–1.2 nm, but are poorly ordered owing to the high solubility of the template. Further increasing the head group size will change the pore symmetries that are obtained due to packing parameter modification.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
3 U. Ceisla and F. Schüth, *Microporous Mesoporous Mater.*, 1999, **27**, 131.
4 P. T. Tanev and T. J. Pinnavaia, *Science*, 1996, **271**, 1267.
5 S. S. Kim, W. Zhang and T. J. Pinnavaia, *Science*, 1998, **282**, 1302.
6 D. Zhao, Q. Huo, J. Feng, J. Kim, Y. Han and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2668.
7 Q. Huo, R. Jeon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.
8 T. Sun and J. Y. Ying, *Angew. Chem., Int. Ed.*, 1998, **37**, 664.
9 D. Zhao, P. Yang, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Commun.*, 1998, 2499.
10 K. J. Balkus, A. G. Gabrielov and N. Sandler, *Mater. Res. Symp. Proc.*, 1995, **368**, 369.
11 A. Galarneau, A. Barodawalla and T. J. Pinnavaia, *Nature*, 1995, **374**, 529.
12 X. Song Zhao, G. Q. Lu and X. Hu, *Chem. Commun.*, 1999, 1391.
13 *Catal. Today*, 1988, **2** (ed. R. Burch).
14 T. W. Davey and A. R. Hayman, *Aust. J. Chem.*, 1998, **51**, 581.
15 T. W. Davey, W. A. Ducker and A. R. Hayman, *Langmuir*, in the press.
16 J. M. Kim, J. H. Kwak, S. Jun and R. Ryoo, *J. Phys. Chem.*, 1995, **99**, 16742.
17 T. W. Davey, W. A. Ducker, A. R. Hayman and J. Simpson, *Langmuir*, 1998, **14**, 3210.
18 V. Hassel, H. Ringsdorf, R. Laversanne and F. Nallet, *Recl. Trav. Chim. Pays-Bas*, 1993, **112**, 339.
19 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
20 A. Galarneau, D. Desplantier, R. Dutartre and F. Di Renzo, *Microporous Mesoporous Mater.*, 1999, **27**, 297.

Communication b000422g