Organomodified hexagonal mesoporous silicates

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A neutral templating route to organically modified silicates with tightly controlled porosity is described. The materials prepared are characterised and compared to the corresponding organofunctionalised silica.

1 Introduction

The discovery of the M41S class of mesoporous silicas by Beck and co-workers in 1992[1,2] has led to the rapid development of a wide variety of regular mesoporous silicates, and other materials, which show promise in catalysis due to their easily controlled and well-defined pore size. A great deal of work has been carried out on the preparation, characterisation and application of these materials as catalysts.

The number of publications on organically modified systems has been significantly lower, despite the current interest in organically modified silicas as catalysts. The majority of these publications involve the post-synthesis modification of preformed MCMs,[3–10] following typical procedures for the grafting of silicas with organo(trialkoxy)silanes. Such materials display higher loading than traditional grafted silicas, and retain the high surface area and pore size distribution of the M41S materials. However, it is to be expected that they might also suffer from the same disadvantages as the grafted silicas, namely little control over loading, relative lack of stability due to partial crosslinking of the silane coupling agent to the silica surface, and the possibility of a variety of surface bound species.[11]

We,[12] and others,[13–16] have therefore developed routes to organically modified M41S-type materials as an alternative approach to these materials, in which the organosilane is copolymerised with the silica precursor in the presence of the templating agent. This variation leads to organomodified materials in one step, where the organic group is incorporated during the condensation of the silica framework, and is therefore likely to be more fully integrated into the material. Since the ratio of the silica precursor to the organosilane can be varied readily, the scope for varying the loading of organic groups is, at least theoretically, much greater. Mann and co-workers[13,14] have published routes to organomodified MCMs using ionic templates, which involves the use of quaternary ammonium salts, a route which has also been used by Stein and co-workers.[15] More recently, Richer and Mercier have published a route based on the use of polyether templates.[16] We have concentrated on the use of the neutral template route of Tanev and Pinnavaia,[17] which utilises long chain amines as the structural agent, and leads to materials designated as hexagonal mesoporous silicas (HMS). Whereas the MCM class of materials have hexagonal long range order, the HMS materials are considerably less ordered and are better described as having wormhole structures.[18] The removal of template is generally considered to be more straightforward in this case than with the quaternary route, which is known to be difficult to remove entirely.[19] We have recently reported both the first preparation of organically modified HMS materials using this route[12] and the first details regarding their performance as catalysts,[20,21] studies which indicated many important advantages over the corresponding silica based materials.

We now wish to report more fully our results on the preparation and properties of organomodified HMS materials, prepared *via* the neutral templating route.

2 Experimental

Tetraethoxysilane (TEOS) was purchased from Aldrich Chemical Company, as was dodecylamine. Silanes were purchased from Fluorochem. Solvents were standard laboratory grade. All chemicals were used as purchased. Distilled water was used throughout.

2.1 Preparation of materials

A typical preparation of an organomodified HMS is as follows: to a stirred solution of *n*-dodecylamine (5.08 g, 27.5 mmol) in aqueous ethanol (46 ml of absolute ethanol and 53 ml of distilled water) at 20 °C was added separately, but simultaneously and rapidly, TEOS (18.8 g, 0.09 mol) and γ-aminopropyl(trimethoxy)silane (1.79 g, 0.01 mol). The cloudy solution was stirred for 18 h. The solution first becomes milky (typically after *ca.* 5 min), then thickens. After 18 h, the thick solution was filtered, and the white solid washed with ethanol. The damp solid product was then refluxed in ten times its weight of ethanol for 3 h and filtered again to remove the template. The solvent reflux was repeated twice to completely remove the template from the material. The final solid was then dried in an oven at 100 °C. Yield = 10.3 g.

An alternative template removal method is to extract the template using a Soxhlet apparatus; 5 h of extraction was sufficient to completely remove the amine.

Aminopropyl-silica, which is used as a representative example of a conventional catalytic material, is prepared by the standard literature method[22] of refluxing silica (Merck Kieselgel 100, 10 g) with γ-aminopropyl(trimethoxy)silane (5.00 g) in toluene (100 ml) for 18 h. The methanol formed was removed periodically by distillation. Filtration and washing with ethanol twice, water twice and ethanol twice, followed by drying yielded the aminopropyl-silica as a white solid with a loading of aminopropyl groups of 0.95–1.00 mmol g^{-1}.

2.2 Characterisation

Materials were characterised by a variety of techniques. Loading was measured using elemental analysis, and for basic

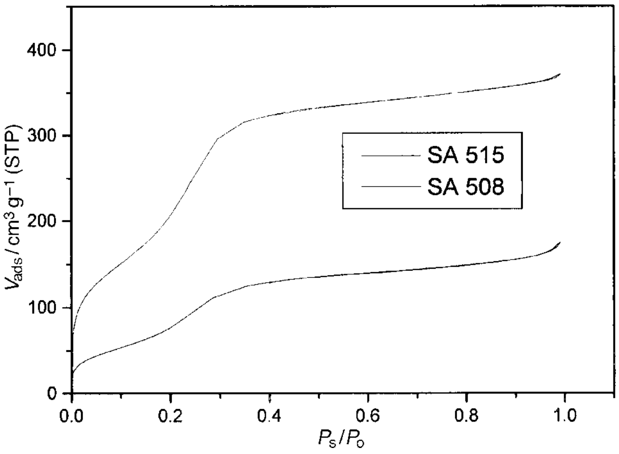

Fig. 1 Adsorption isotherms of organically modified HMS materials. SA 508 is 1.1 mmol g^{-1} aminopropyl-HMS and SA 515 is 1.1 mmol g^{-1} cyanoethyl-HMS.

compounds, titration was also employed to determine the number of basic sites. The physical structure of the materials was investigated using dinitrogen adsorption isotherms, scanning electron microscopy and tunneling electron microscopy.

Adsorption isotherms were carried out using a Coulter SA3100 Instrument. Reichardt's dye polarity measurements[23,24] were derived from diffuse reflectance UV–VIS spectra, which were carried out on a Perkin Elmer Lambda 15 spectrophotometer. Solid state NMR spectra were carried out on a Bruker MSL300 NMR spectrometer operating at 59.63 MHz.[25] Scanning electron microscopy used a Hitachi S-2400 microscope and transmission electron microscopy used a JEOL JEM 1200EX instrument. X-Ray diffraction was carried out on a Philips 1050 using Cu Kα.

3 Results

3.1 Scope of the method

The formation of organically modified silicate materials with structures typical of the HMS materials described by Tanev and Pinnavaia has been successfully achieved with a variety of different silanes. Typical adsorption isotherms are shown in Fig. 1. Both basic and non-basic silanes were successfully utilised in the preparation of ordered HMS materials, with the amine containing silanes consistently giving lower surface areas than the non-basic silanes, although pore size distributions did not vary between the two groups of silanes. The structural characteristics of these materials are summarised in Table 1. The synthesis conditions are such that almost all the silicon containing precursors are incorporated at ratios of organosilane : TEOS of 1 : 4 or less, leading to loadings approaching the theoretical. Higher proportions of organosilane rarely give ordered materials. While the loadings of these disordered materials can be very high (approaching 4 mmol g^{-1} in some cases),[26] the quantity of insoluble material obtained in others is often low, indicating the formation of soluble polymers. These materials are currently being investigated and will be discussed in a separate article.

3.2 Polarity measurements

The use of Reichardt's dye as a probe of solution polarity has recently been extended to solid surfaces.[23,24] Reichardt's dye measurements were made on a range of organically modified HMS materials, according to the literature procedure. The resulting E_T^N values are tabulated in Table 1, along with some relevant comparative data. What can be seen from the data is that the 1 mmol g^{-1} samples all have a high polarity, approaching that of the purely siliceous material. While functionalised silicas display a significant drop in polarity with even low loadings[23,24] the HMS materials are significantly more polar, and much higher loadings are required before the average surface polarity drops significantly. This is no doubt a consequence of the much higher surface area of the HMS materials. The alkylamino functions display a significantly greater reduction in polarity than the primary amine derivatives.

3.3 Scanning electron microscopy and transmission electron microscopy

Scanning electron microscopy was carried out on the materials generated, and representative photographs are shown in Fig. 2. As can be seen, the materials consist predominantly of two morphologies. The major proportion of the material is made up of aggregates of smaller roughly spherical particles, whose dimensions are of the order of 0.4–1.5 µm [Fig. 2(a)], the average size of the aggregates being 30–75 µm or larger [Fig. 2(b)]. A second type of structure consists of single particles, again roughly spherical, but of a much larger size, typically 20–40 µm. Some of these are aggregated into groups of two or three, but not into larger aggregates. A small quantity of angular amorphous particles is also apparent. No SEM data appears to have been published on HMS materials, but the morphology seen here is significantly different to that seen for the related MCM materials, which occur as hexagonal particles.[1,2] The spherical structures present are often seen in a range of mesostructured materials.

Transmission electron microscopy reveals the presence of porosity, but indicates little long range order. Pore size

Table 1 Physical parameters of templated materials

Organic	Loading/mmol g^{-1}	Template	Surface area/m^2 g^{-1}	Pore size[a]/nm	E_T^N
$H_2N(CH_2)_3$–	1.1	C_{12}	756	3.6	0.90
$H_2N(CH_2)_3$–	2.4	C_{12}	745	3.7	0.82
$H_2N(CH_2)_3$–	3.0	C_{12}	715	3.6[b]	0.74
$MeHN(CH_2)_3$–	1.1	C_{12}	731	3.6	0.75
$Me_2N(CH_2)_3$–	1.1	C_{12}	925	3.6	0.75
$Me_2N(CH_2)_3$–	2.3	C_{12}	707	3.3	0.68
$H_2N(CH_2)_2NH(CH_2)_3$–	1.2	C_{12}	649	3.5	0.85
$Cl(CH_2)_3$–	1.1	C_{12}	1607	3.9	0.86
$NC(CH_2)_2$–	1.1	C_{12}	1356	3.7	0.87
$CH_2{=}CH$–	1.2	C_{12}	1056	3.6	0.87
Silica (Kieselgel 100)	—	—	254	8[c]	0.96
Propylamine	—	—	—	—	0.19
$[SiO_2](CH_2)_3NH_2$	1.0	—	207	8[c]	0.56

[a] Pore sizes were measured using the geometrical model, in which the average pore diameter is equal to $4V/S$, where V is the pore volume and S is the specific surface area, except for 3.0 mmol g^{-1} aminopropyl-HMS, where the pore size is given as the maximum in the adsorbed volume *vs.* pore size plot. [b] Partially templated; also contains some amorphous material. [c] Amorphous silica with broad pore size distribution.

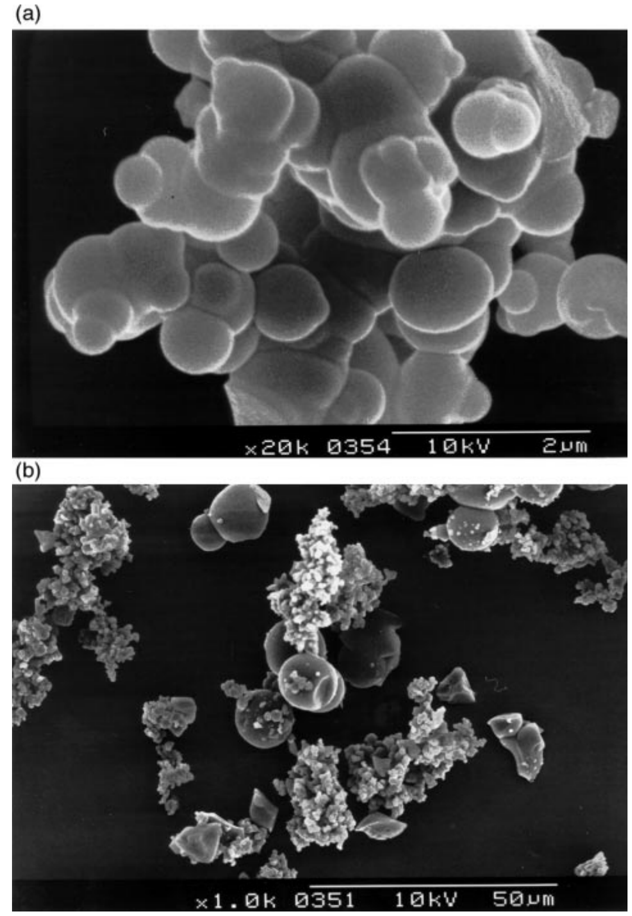

Fig. 2 SEM photographs of 1.1 mmol g^{-1} aminopropyl-HMS; (a) 20 000 × magnification, (b) 1000 × magnification.

appears uniform, but there are no regions which display long range regular pore structures (Fig. 3), as is occasionally seen in MCM type materials. However, such features are rarely seen in HMS materials. No lamellar material was observed. There is evidence that some particles consist of approximately hexagonal platelets which exist as semiregular aggregates [Fig. 3(b)]. The dimension of the side of the hexagon is *ca.* 100 nm.

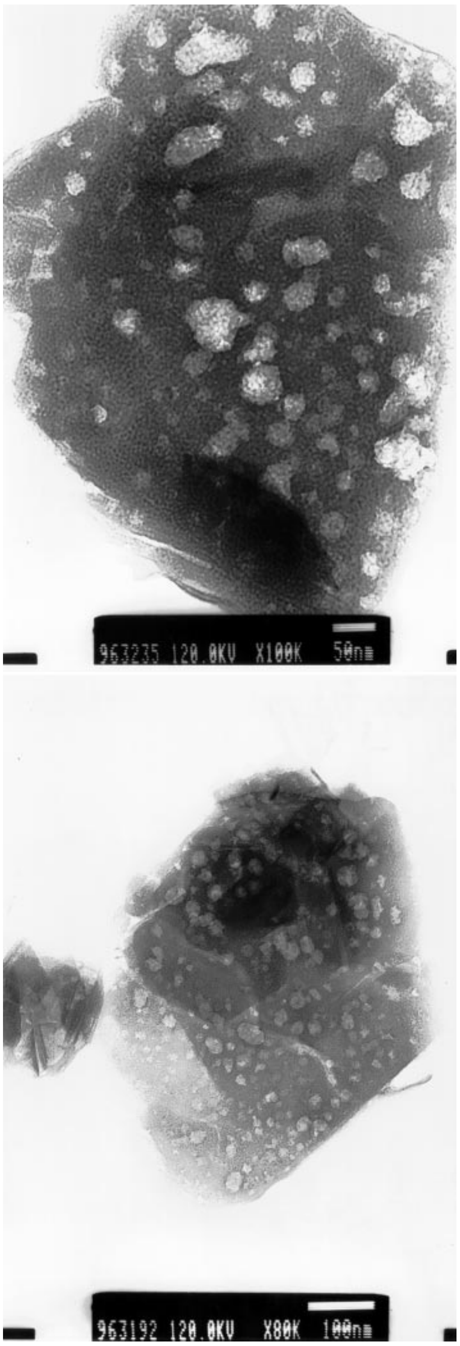

Fig. 3 TEM photograph of 1.1 mmol g^{-1} aminopropyl-HMS material showing the typical wormhole pattern; (a) 100 000 × magnification, (b) 80 000 × magnification.

3.4 X-Ray Diffraction

X-Ray diffraction patterns were measured for two samples. In all cases, patterns were lacking in detail, and did not display higher order reflections. The only reflection observed was broad and centred on 4.2 nm for both 1.1 mmol g^{-1} aminopropyl-HMS and 1.1 mmol g^{-1} cyanoethyl-HMS. As is expected, these HMS materials do not display the degree of long range order associated with the MCM-41 class of silicates.

Table 2 Results of deconvolution analysis of the ^{29}Si CP MAS NMR spectra of 1.1 mmol g^{-1} aminopropyl-HMS, 1.0 mmol g^{-1} aminopropyl-silica and 1.1 mmol g^{-1} cyanoethyl-HMS

Chemical shift (δ)	Assignment	Relative amount (%)
Aminopropyl-HMS (1.1 mmol g^{-1})		
-63.1	T2	24
-68.3	T3	76
-96.6	Q2	11
-101.9	Q3	50
-109.9	Q4	39
Cyanoethyl-HMS (1.1 mmol g^{-1})		
-63.1	T2	26
-68.7	T3	74
-96.4	Q2	11
-102.0	Q3	49
-109.8	Q4	40
Aminopropyl-silica (1.0 mmol g^{-1})		
-57.0	T1	49
-66.2	T2	51
-96.3	Q2	2
-100.7	Q3	36
-109.9	Q4	62

3.5 Thermal analysis

The TGA traces of aminopropyl-HMS and aminopropyl-silica are shown in Fig. 4. Thermal analysis of the AMP-HMS material showed one main weight loss in the range 400–650 °C. This is due to loss of the organic groups from the surface. A smaller weight loss is seen at lower temperatures, and is due to the loss of water from the surface (*ca.* 0.75% between 100 and 400 °C). On runs up to 1000 °C, continued weight loss was minimal beyond 650 °C and may be due in

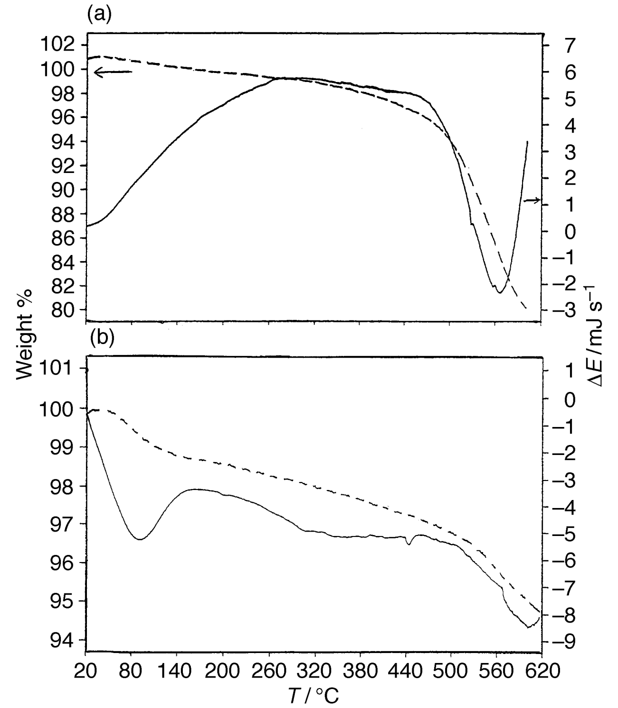

Fig. 4 Thermal analysis profile of (a) 1.1 mmol g^{-1} AMP-HMS and (b) 1.0 mmol g^{-1} AMP-silica. Profiles shown over the range 20–625 °C.

part to residual organic material, and to loss of hydroxy groups from the surface by condensation to give siloxanes. No DSC events were seen within this temperature range.

The amount of weight loss due to the aminopropyl groups (7.2%) corresponds to a loading of 1.2 mmol g^{-1}, in excellent agreement with other analytical techniques.

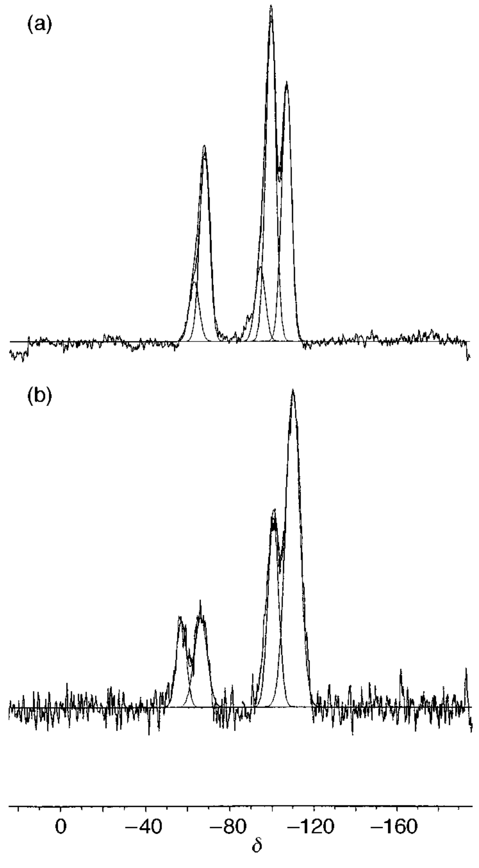

Fig. 5 ^{29}Si CP MAS NMR spectra of (a) 1.1 mmol g^{-1} aminopropyl-HMS and (b) 1.0 mmol g^{-1} aminopropyl-silica.

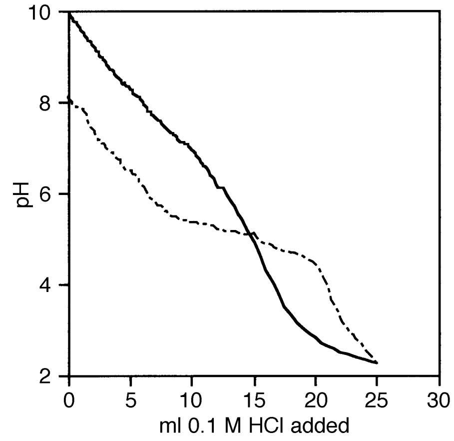

Fig. 6 Potentiometric titration of 1.1 mmol g^{-1} AMP-HMS (— - — -) and (b) 1.0 mmol g^{-1} AMP-silica (———).

The corresponding weight loss from the AMP-silica material is much less well defined. There is a gradual drop in weight from 100 to 260 °C (*ca.* 0.8%). The second weight loss, which begins at *ca.* 290 °C and continues to 625 °C, corresponds to the loss of aminopropyl groups from the surface. The weight loss in this range is 5.2%, corresponding to a loading of 0.95 mmol g^{-1}, fitting in well with the results of other loading analyses. Above this temperature almost no weight loss is observed up to the final temperature of 1000 °C.

The higher temperature at which loss of aminopropyl groups occurs in the HMS material, and the wider temperature range in which it occurs, indicates that the organic groups are more strongly bound to the surface in the silica material, and that there is a narrower spread of different organic sites on this material.

3.6 ^{29}Si NMR of materials

The ^{29}Si CP MAS NMR spectra of 1.1 mmol g^{-1} aminopropyl-HMS and 1.1 mmol g^{-1} cyanoethyl-HMS were measured, as was the spectrum of 1.0 mmol g^{-1} aminopropyl-silica, with a contact time of 8 ms. Under these conditions, the spectra should be a good reflection of the surface concentrations of the various silica species present.[25]

The spectra were deconvoluted and the relative areas of the various peaks displayed in the spectra for both the HMS materials are very similar, both in terms of the chemical shifts of the various silicon species, and the relative amounts (Table 2). For this reason, Fig. 5 displays the spectra obtained for aminopropyl-HMS and aminopropyl-silica. The similarity of the spectra for the aminopropyl- and cyanoethyl-HMS materials would indicate that the amino group in the aminopropyl silane does not play a significant role in defining the extent or nature of attachment of the silanes by catalytic hydrolysis/condensation sequences, as is postulated for aminopropyl silicas.[11] Given the large amount of basic template, and that the probable condensation mechanism involves condensation at the amine-rich interface of the templating solution, it is perhaps not surprising that the presence of a relatively small amount of additional amine has little effect.

A comparison of the T peaks (due to the silane reaction partner) indicates that the silane is much more robustly bound in the case of the directly prepared HMS materials than the post-modified silica. Thus, the silanes in the HMS materials form an integral part of the surface of the material, whereas the much less complete binding of the post-modified material indicates a less well incorporated functionality. It should be noted that this comparison is valid for the two materials discussed here, which have very similar loadings of aminopropyl groups. However, it is possible to increase the degree of condensation of a silane to a silica surface by carrying out the grafting in aqueous environments. Under these conditions, the total loading achieved by post-modification of the silica is significantly lower than for the toluene method, and oligomerisation of the aminopropylsilane also takes place.[27]

3.7 Potentiometric titration

Potentiometric titration of AMP-HMS (1.1 mmol g^{-1}) and AMP-silica (0.95 mmol g^{-1}) was carried out by addition of 0.01 M HCl to a stirred suspension of the material in deionised water at room temperature. After the addition of 0.2 ml acid, the system was allowed to equilibrate over a 2 h period until a pH of 2.4 was obtained. The titration curves are shown in Fig. 6.

As can be seen, the silica-derived material contains sites which are more basic, but also has a very wide distribution of different sites. The AMP-HMS, on the other hand, has a much narrower range of sites, of relatively low basicity.

4 Discussion

The copolymerisation of tetraethoxysilane and organo(trialkoxy)silanes in micellar amine solutions provides a direct route to organofunctionalised materials. The removal of template is easy and is complete after triple extraction with refluxing ethanol, or after a few hours of Soxhlet extraction. The products are fine powders which display very high surface areas (*ca.* 700–1600 m^2 g^{-1}) and narrow pore size distributions. The pore sizes found are independent of the amount and nature of the organosilane used. This value is significantly larger than that obtained with wholly siliceous HMS,[17] where the template is removed by calcination. Values found for quaternary templated organomodified MCMs are only available for samples with hexadecyltrimethylammonium bromide template,[13,14] but the pore size of these materials is dependent on the ratio of organosilane to TEOS, a phenomenon not seen in the case of the neutral template, where pore size is not affected significantly by this ratio. This may be due to the more hydrophilic solvent used in the MCM preparation causing some of the hydrophobic organosilane to exist within the templating micelles, leading to expansion of the micelle with increasing organosilane concentration. Such a phenomenon would be less likely to occur in the more organophilic solvent system used in this work, and consequently, the pore size distribution is more predictable, and the loading is higher.

A variety of silanes has been successfully incorporated. Both basic and non-basic silanes can be used, with the basic, amine-containing silanes consistently giving lower surface areas than the neutral materials.

Several differences between these materials and the equivalent functionalised silicas are evident. Variation of the ratio of silanes allows control over loading. We have found that loadings of up to 2.4 mmol g^{-1} are possible, and that the materials formed have the high surface areas and pore size distributions typical of HMS materials. Higher ratios of organosilane to TEOS lead to higher loadings (up to 3.8 mmol g^{-1} have been achieved[27]), but the products are at best partially templated or, more usually, completely amorphous. This can be compared with the loadings achieved by grafting organosilanes onto silicas, where loadings are never higher than 1 mmol g^{-1}, and are often <0.5 mmol g^{-1}. Higher loadings are achievable by grafting organosilanes onto MCMs[28] but still do not reach the levels achievable by the direct method.

The stability of the bound groups is also higher than for silicas. Thermal analysis indicates that loss of organic groups starts at *ca.* 400–450 °C, depending on the sample, and continues until *ca.* 700 °C. The stability of the equivalent groups attached by grafting onto silica is significantly lower, with (probably physisorbed) material typically being lost at temperatures as low as 250 °C. Furthermore, ^{29}Si NMR of the solid indicates that the degree of attachment of the silane to the framework is much more complete. Approximately 75% of the silane groups are attached by three Si—O—Si bonds, with the remainder being attached by two. Again, the binding of grafted organosilanes to silica is much less complete, with typical degrees of attachment being *ca.* 50% *via* one Si—O—Si unit, and *ca.* 50% *via* two. These results indicate that the templated materials contain negligible quantities of physisorbed silanes, and that the bound groups are thermally and solvolytically stable.

Polarity measurements of the surface of the modified HMS materials indicate that the surfaces are more polar than those of functionalised silicas, and that there is little difference between the polarity of the functional materials and that of the unfunctionalised HMS materials.[23,24] This is probably due to the much higher surface areas, leading to a large amount of unfunctionalised surface being available. Very high loadings of organic groups do reduce the polarity to some extent.

The basicity of the aminopropyl-HMS system is quite low, and there appears to be a significant degree of uniformity in the basic strength of the groups. This is in contrast to the wide range of different sites found in the post-modified materials. The preformed surface of silica has a range of different sites, which will interact with the incoming silane in a variety of ways, leading to a range of different bound groups. The difference in the HMS materials is currently the subject of further investigation, but may indicate the formation of a specific surface precursor during the early stages of hydrolysis, which becomes incorporated in the surface. The titration behaviour indicates a pK value approximately that of a silanol in silica, leading to the possibility that ion pairing between the amino group and a partially hydrolysed $(EtO)_{4-n}Si(OH)_n$ species may occur. The basic site on the aminopropyl-HMS material may thus resemble $NH_3^+\cdots{}^-OSi$. Investigations into this phenomenon are ongoing and will be reported separately in due course.

5 Conclusions

Neutral templating provides a simple and versatile method for the production of organically functionalised silicas with tightly controlled porosity and very high surface area. The loading of organic groups can be varied over a large range and can be easily controlled by adjusting the ratio of silanes in the system. Loadings can be as high as 3 mmol g^{-1} in a few cases, but higher loadings produce amorphous materials. The organic groups are robustly bound to the silicate structure and appear to be more uniform in nature than those obtained by post-treatment of silica.

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