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Organically modified hexagonal mesoporous silicas (HMS)—remarkable effect of preparation solvent on physical and chemical properties

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The preparation of a series of aminopropyl-substituted micelle templated silicas is presented, in which the materials are synthesised by a one-step co-condensation route using dodecylamine as template. The effect of solvent composition on the material properties, reactivity and catalytic activity is discussed. Increasing the water content of the preparation solvent causes an increase in the framework pore diameter, and, at high water contents, a great deal of textural porosity is seen. Particle size does not change over the range studied, in contrast to other micelle templated silica systems published recently. However, two materials, prepared at intermediate solvent compositions have very different morphology, and curiously, very different reactivities as nucleophiles. Their catalytic activity in the Knoevenagel reaction does however follow the same trend as for all the other samples. The processes occurring are discussed.

Introduction

The discovery of the M41S family of silicas in 1992[1,2] has led to an enormous quantity of work in the field of templated synthesis of mesoporous materials. A consequence of this is the wide range of structures which are currently available *via* numerous variations on the principle.[3–9] A variety of templates has been used successfully,[4,9,10] including charged (cationic[1,2] and anionic[9,10] surfactants) as well as neutral (amines,[5] diamines,[11] alkylated polyethers[6]), all of which lead to highly structured silicas and substituted silicas. Furthermore, not only can the original silicas and aluminosilicates be prepared, but access to many templated oxides displaying high surface areas and narrowly defined porosity is now possible.[9,10] Elegant approaches such as ligand-assisted templating have been introduced by Ying and co-workers as a method of encouraging otherwise reluctant monomers to self-assemble and condense to give mesoporous and highly structured materials.[12,13] Many metal-substituted silicas are now also available *via* these processes as are several metal oxides. Applications of these materials include catalysis[14] as well as metal ion extraction,[15,16] adsorption[17] and sensors.[18]

A particularly interesting route to organic–inorganic hybrid materials has been the extension of the templating methodology to allow the inclusion of organic groups during the sol–gel processing stage.[19–30] The above references show that several of these have already shown excellent activity as catalysts in a range of applications, indicating that these materials show great promise.

While a great deal of work has been published relating to the effect of preparation conditions on the structural characteristics and catalytic activity of materials derived from the quaternary ammonium directed templating route to MCM-41 and others, considerably less has been discovered about other preparative routes. This is despite the great promise and flexibility offered and already demonstrated by these methods, in particular the neutral amine templating route first announced by Tanev and Pinnavaia.[5] This route allows a wider range of metals to be incorporated in the framework of the materials than other routes.[31,32] Also, the ease of template removal compared to the ionic routes allows the removal of template under very mild conditions, while preserving delicate organic functions within the material.

Pinnavaia and co-workers have studied the effect of solvent on the physical structure and catalytic activity of silica and aluminium-doped silicas (HMS) prepared by their neutral templating method.[33,34] They found that more water-rich environments favoured the development of significant textural porosity (as defined by a step in the nitrogen adsorption isotherm at high partial pressures), larger framework mesopores (as defined by the step at lower partial pressures), and much smaller particles. They found that water–alcohol mixtures (methanol, ethanol, propanol) which dissolved the 1-aminododecane template gave materials with very little textural mesoporosity. On the other hand, solvent systems which did not form a homogeneous solution before addition of the silanes always gave materials with large textural pore volumes, often greater than the framework pore volumes. This textural porosity has been invoked as being responsible for the enhanced catalytic performance of many materials.[34–40] Furthermore, they found that the size of the particles formed was substantially smaller in water rich conditions. These differences were attributed to the more rapid hydrolysis and nucleation rate producing more and smaller primary particles in high water solvents, and their formation and growth at the surfaces of colloidal surfactant lead to the high level of textural porosity.

Di Renzo *et al.*[41] studied both MCM-41 and HMS materials and found similar results. In the case of MCM-41, the particle size is strongly affected by the rate of hydrolysis, with slower hydrolysis giving larger particles. Water rich solvent systems produced materials with higher degrees of textural porosity and larger framework mesopore diameters, the latter being attributed to the influence of ethanol co-surfactancy in the micelles in ethanol rich systems leading to a reduction in pore size.

We now wish to present our results concerning the effect of solvent on the preparation of a representative organic–inorganic hybrid material prepared *via* a one step co-polymerisation using the HMS system.[42] We also include details of the unusual and unexpected reactivity and activity of the organic groups in both stoichiometric and catalytic reactions. These results indicate that, at least in this case,

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changes in activity can be related to changes in the nature of the active site, the framework pore size, and not just to textural porosity.

Experimental

Ethanol was obtained from Fisher (HPLC grade). Deionised water was used in all the preparations. The silanes tetraethoxysilane (TEOS) and 3-aminopropyltrimethoxysilane (AMP–silane) were obtained from Fluorochem and used without further purification. All other chemicals were obtained from Aldrich and were used without further purification, with the exception of benzaldehyde, which was purified by reaction with neutral alumina to remove any acid formed by oxidation, followed by distillation under nitrogen.

Analysis

CHN analysis was obtained from UMIST, Manchester, UK. Nitrogen porosimetry was obtained on a Coulter SA3100 instrument. Scanning electron microscopy was performed on a Hitachi S-2400 instrument. Reactions were followed using a Hewlett-Packard 6890 GLC (DB-5 column). Conversions were calculated using *n*-dodecane as internal standard.

Preparation of aminopropyl–HMS materials

The standard preparation of these materials was adapted from the published procedure,[21] using a 9 : 1 molar ratio of TEOS : AMP–silane. The total amount of silane was kept at 0.1 mol. The total solvent mass was 100 g. The quantity of *n*-dodecylamine used was 5.10 g (0.030 mol). Solvent proportions were varied in the range 25 g water : 75 g ethanol to 75 g water : 25 g ethanol. A representative preparation is as follows:

TEOS (18.72 g, 0.09 mol) and AMP–silane (1.79 g, 0.01 mol) were added separately, but simultaneously, over a few seconds, to a stirred solution of *n*-dodecylamine (5.10 g, 0.030 mol) in 50 g ethanol and 50 g water. The temperature of the reaction was ambient (20 ± 2 °C) unless otherwise stated. Typically a slight exotherm (2–3 °C) was noted. The reaction was stirred for 18 h, the solid formed was filtered and sucked dry, before being extracted with absolute ethanol in a Soxhlet apparatus for 8 hours. The resultant solid was then dried at 100 °C for 16 hours. Materials are referred to as AMP–HMS–*x*W where *x* refers to the mass percentage of water (W) in the solvent mixture.

Catalytic activity of the materials

Ethyl cyanoacetate (2.26 g, 20 mmol) and 3-pentanone (1.92 g, 20 mmol) were added to a refluxing suspension of material (0.25 g) in toluene (35 ml). The reaction vessel was stirred magnetically, and a Dean–Stark trap was attached to continuously remove the water formed during the reaction. *n*-Dodecane was also present (0.3 g) as an internal standard. Samples were taken at regular intervals, filtered and diluted by a factor of 5 : 1 with dichloromethane and analysed by GC, with products being confirmed by GC-MS, and by isolation using standard procedures. Details of the catalytic activity of the 53.5W material have already been published.[23,24]

An identical procedure was followed for the reactions with cyclohexanone and benzaldehyde.

Stoichiometric reaction with benzaldehyde

The material (0.500 g) was added to 10 ml of cyclohexane containing *n*-dodecane (0.30 g) and benzaldehyde (0.106 g, 1 mmol). The reactions were stirred at 20 °C and samples (0.1 ml) taken at appropriate intervals, filtered and the material washed with ethanol (0.5 ml). The filtrate was then analysed by GC, and the loss of benzaldehyde compared to a sample taken before addition of the material. Identical results could be obtained by monitoring using UV-visible spectroscopy. Infrared spectroscopy confirmed the lack of free benzaldehyde on the surface of the washed material, the only additional band around 1600–1700 cm^{-1} being the characteristic imine stretching vibration at 1642 cm^{-1}.

Table 1 Carbon and nitrogen contents of the materials prepared

Sample	Carbon/ mmol g^{-1}	Nitrogen/ mmol g^{-1}	C : N ratio
AMP–HMS–25W	6.81	1.21	5.6
AMP–HMS–35W	6.62	1.22	5.4
AMP–HMS–45W	7.40	1.23	6.0
AMP–HMS–50W	7.59	1.20	6.3
AMP–HMS–53.5W	9.00	1.25	7.2
AMP–HMS–60W	7.62	1.17	6.5
AMP–HMS–65W	8.20	1.14	7.2
AMP–HMS–75W	7.44	1.31	5.6

Results

Elemental analysis

The results of the elemental analyses for the materials prepared are essentially invariant with change in the solvent mixture used in the preparation. The compositions are given in Table 1. As can be seen, the number of aminopropyl groups incorporated is constant at *ca.* 1.2 mmol g^{-1}, a figure which indicates essentially complete incorporation of aminosilane. The C : N ratio significantly exceeds the theoretical value of 3. Spectroscopic evidence indicates that this is due to unhydrolysed ethoxy groups remaining in the structure. No methoxy groups are evident, indicating that, as expected, the more reactive methoxy groups are lost preferentially, leaving the less reactive (and much more plentiful in the synthesis mixture) ethoxy groups in the structure. Elemental analysis indicates that the number of ethoxy groups is roughly constant for all the materials, at around 1.5 ethoxy groups per aminopropyl chain, or 1.5 ethoxy groups per 10 silicon atoms.

Scanning electron microscopy

The analysis of the materials by scanning electron microscopy indicates several interesting features. Representative images are displayed in Fig. 1, and the findings are briefly summarised in Table 2. Firstly, the particle morphology is essentially constant across the range of solvents used, except for AMP–HMS–53.5W and AMP–HMS–50W, with intergrown spherical particles being essentially the only form seen. The degree of intergrowth is possibly slightly higher in the high water samples than in those prepared in ethanol rich conditions. The particle size is essentially invariant at *ca.* 0.5–1.1 µm across all the solvent mixtures studied except for AMP–HMS–50W and AMP–HMS–53.5W. This is in stark contrast to both the MCM-41 and all-silica HMS studies previously carried out.[33,34,41] In these studies the particle size was strongly affected (by approximately an order of magnitude) by the solvent composition.

A striking exception are those materials prepared in solvents with approximately equal amounts of ethanol and water (samples AMP–HMS–50W and –53.5W). These materials display mixed morphologies, with some particles exhibiting the spherical morphology and size distribution of the other materials (Fig. 1b). However, the predominant morphology in these samples is amorphous, with large irregular particles ($>$10 µm) being common. Clusters of very small particles ($<$0.1 µm, again amorphous) can also be seen.

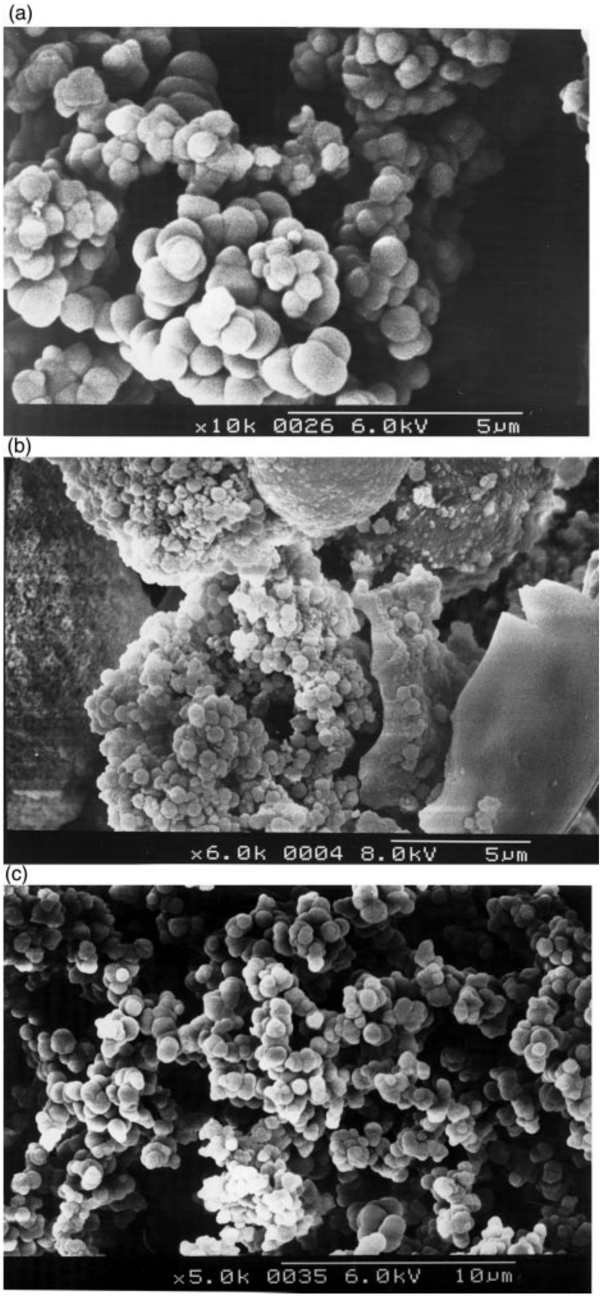

Fig. 1 Scanning electron micrographs of selected materials. The upper image (a) is of AMP–HMS–25W, the central image (b) is of AMP–HMS–50W and the lower image (c) is of AMP–HMS–70W.

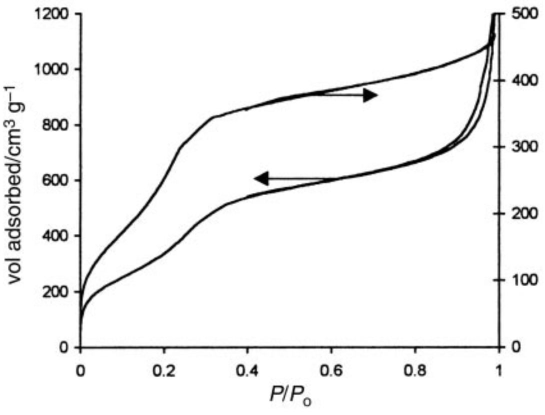

Fig. 2 Nitrogen adsorption isotherms of two selected materials; the left hand axis represents AMP–HMS–60W, prepared in an initially heterogeneous solution and the right hand axis AMP–HMS–40W, prepared in an initially homogeneous solution. The volumes adsorbed refer to *gaseous* nitrogen.

Nitrogen adsorption data

The results of the nitrogen adsorption measurements are displayed in Table 2, and representative isotherms are shown in Fig. 2. As can be seen from these data, the surface area of the materials varies between 635 and 914 $m^2 g^{-1}$, values typical for such hybrid materials, and *ca.* 20–40% lower than that normally seen for HMS and MCM–41 materials. There is no distinct trend, but it is possible that the surface areas become slightly lower at high water contents, consistent with Pinnavaia's study.[34]

Values for framework pore volume (defined as the *liquid* volume of nitrogen adsorbed at $P/P_0 \leqslant 0.5$) increase steadily from 0.33 to 0.50 $cm^3 g^{-1}$ as the water content of the solvent increases. These values are again typical for AMP–HMS materials, and are somewhat lower than those reported for MCM and HMS materials. For example Di Renzo[41] reported that the total pore volume increased from solvent compositions 30 vol% water to 70 vol% water, starting at 0.49 $cm^3 g^{-1}$ and reaching 0.86 $cm^3 g^{-1}$. Representative isotherms indicate that in the low water compositions, the vast majority (*ca.* 95%) of the total pore volume is framework-confined, whereas, in higher water systems, 80–90% of the total is framework-confined. Pinnavaia reported framework pore volumes of 0.73 to 0.90 $cm^3 g^{-1}$ in his study.[34]

The textural pore volume (volume adsorbed at $P/P_0 > 0.5$) is extremely low at low water contents, and increases gradually until the templating solution becomes heterogeneous (at *ca.* 60 vol% water). After this point the textural pore volume increases dramatically, reaching a remarkable value of

Table 2 Structural parameters relating to the materials prepared

Sample	Surface area/$m^2 g^{-1}$	$V_{fp}{}^a/cm^3 g^{-1}$	D_{fp}/nm	$V_{tp}{}^a/cm^3 g^{-1}$	SEM details
AMP–HMS–25W	810	0.328	1.6	0.037	Spherical particles 0.5–1.1 μm
AMP–HMS–35W	914	0.360	1.6	0.038	Spherical particles 0.7–1.2 μm
AMP–HMS–45W	883	0.441	2.0	0.038	Spherical particles 0.5–1.0 μm
AMP–HMS–50W	793	0.459	2.3	0.043	Spherical particles 0.5–1.1 μm and very large irregular particles (>10 μm) and very small clusters of irregular particles (<0.1 μm)
AMP–HMS–53.5W	721	0.439	2.4	0.076	Spherical particles 0.7–1.3 μm and very large irregular particles (>10 μm) and very small clusters of irregular particles (<0.1 μm)
AMP–HMS–60W	707	0.458	2.6	0.783	Spherical particles 0.5–1.0 μm
AMP–HMS–65W	635	0.443	2.7	1.465	Spherical particles 0.5–1.2 μm
AMP–HMS–75W	670	0.503	3.0	2.012	Spherical particles 0.6–1.1 μm

[a] V_{fp} = Framework pore volume, V_{tp} = textural pore volume, D_{fp} = framework pore diameter. The volumes tabulated here are based on the volume of liquid nitrogen adsorbed in the ranges $P/P_0 < 0.5$ (V_{fp}) and $P/P_0 > 0.5$ (V_{tp}).

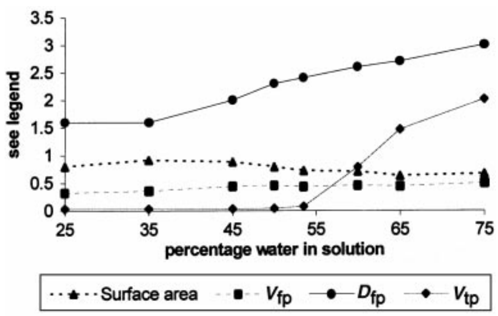

Fig. 3 Physical parameters of the various materials (see also Table 2). The x-axis represents the percentage water in the synthesis solution; thus 25 represents the material AMP–HMS–25W; 75 the material AMP–HMS–75W. The y-axis scales are as follows: Surface area, S (1000 m^2 g^{-1}); V_{fp}—Framework pore volume (cm^3 g^{-1}); D_{fp}—Framework pore diameter, measured by the ratio $4V(l)_{fp}/S$ (nm), where $V(l)_{fp}$ is the volume of *liquid* nitrogen adsorbed in the pores at $P/P_0 < 0.5$; V_{tp}—Textural pore volume (cm^3 g^{-1}) from the pore volume at $P/P_0 > 0.5$.

2.01 cm^3 g^{-1} at the highest water content studied. This is in line with the observations of Pinnavaia[34] who ascribed this sudden change to nucleation and growth of particles taking place at the interface of colloidal particles of surfactant in the templating mixture, leading to greater intergrowth and the development of textural porosity. The results of this study are summarised graphically in Fig. 3.

Temperature studies have also been carried out on two materials—AMP–HMS–50W and AMP–HMS–60W (Table 3). Similar trends were noted in both cases, although the temperature range available was limited, due to the weak template-growing silica interactions being easily disrupted. Thus, AMP–HMS–50W gave structured materials between 0 and 50 °C with higher temperature preparations giving only amorphous solids. AMP–HMS–60W was more restricted, in that only 0 and 20 °C gave structured materials, with higher materials being amorphous. The reasons for this appear to be that one of the major effects of increasing the temperature is to increase the amount of textural porosity—this indicates that the macroscopic structure of the materials is less intact; such materials may be more susceptible to collapse either during synthesis, or during template extraction. A second change which was noted was that the framework pore size is larger at low temperatures. While the reasons for this are not clear, the phenomenon does allow some increase in the pore size range achievable by this method (standard micelle-swelling methods[1] have not yet proved successful with these materials).

Reaction studies

The resultant materials were used as catalysts in the Knoevenagel reaction of ethyl cyanoacetate and benzaldehyde, cyclohexanone or 3-pentanone. These reactions have been previously used to evaluate aminopropyl-containing materials as basic catalysts.[23,24,43] A second reaction, the condensation of the amine function with benzaldehyde to give the imine can be used as a qualitative measure of the nucleophilicity of the amine group. This type of reaction has been used to anchor catalytically active groups to silica-bound aminopropyl functions.[44–46] The reactions investigated are shown in Fig. 4.

Table 3 Temperature effects on AMP–HMS formation

Sample	Surface area/m^2 g^{-1}	$V_{fp}{}^a$/cm^3 g^{-1}	D_{fp}/nm	$V_{tp}{}^a$/cm^3 g^{-1}	T/°C
AMP–HMS	496	0.42	3.1	0.06	0
–50W	793	0.46	2.3	0.04	20
	656	0.34	2.1	0.24	50
	360		Not templated		80
AMP–HMS	935	0.73	3.1	0.44	0
–60W	707	0.46	2.6	0.78	20
	502		Not templated		50

[a] The volumes tabulated here are based on the volume of liquid nitrogen adsorbed in the ranges $P/P_0 < 0.5$ (V_{fp}) and $P/P_0 > 0.5$ (V_{tp}).

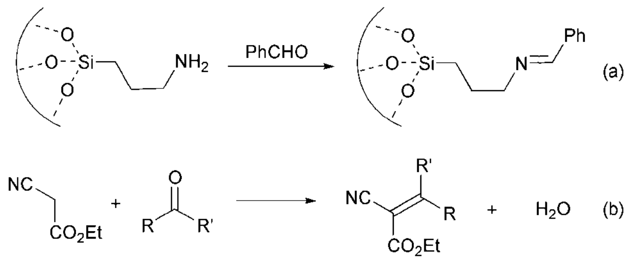

Fig. 4 Reactions used to probe the reactivity and activity of the materials prepared as a function of solvent composition. Reaction (a) is the stoichiometric reaction between benzaldehyde **1** and the amino function, which indicates the nucleophilicity of the nitrogen centre; reactions (b) are catalytic reactions using the materials. Three different carbonyl components were chosen to react with ethyl cyanoacetate **4** to represent varying levels of reactivity with respect to the carbonyl component. The first is with benzaldehyde (**1**, R = Ph, R′ = H), the second cyclohexanone (**2**, R + R′ = $(CH_2)_5$) and the third 3-pentanone (**3**, R′ = R = Et).

Catalytic reactions

The Knoevenagel reaction of aldehydes or ketones with ethyl cyanoacetate is one of the classical test reactions of liquid phase base catalysis. Several studies have been carried out on the condensation of ethyl cyanoacetate and benzaldehyde.[47–56] The reaction of aldehydes in this reaction is significantly faster than the reaction with ketones, with both electronic and steric effects being important,[57] and the materials described in this paper are amongst the few effective catalysts for the condensation of ketones. Our interest in the unusual properties of the materials described here was aroused by our first catalytic experiments with the AMP–HMS–53.5W material, which was extremely poor in the condensation of benzaldehyde with ethyl cyanoacetate but, remarkably, much more active with ketones as reactants.[23] Even the extremely sluggish acetophenone reacted more rapidly than benzaldehyde, a situation unprecedented as far as we are aware in the long history of the Knoevenagel reaction. This prompted us to investigate the effects of preparation conditions on the activity of the materials. The results are displayed in Fig. 5.

As can be seen the rate of the Knoevenagel condensation of cyclohexanone **2** with ethyl cyanoacetate **4** follows an irregular pattern, but one which roughly follows the trend in *framework*

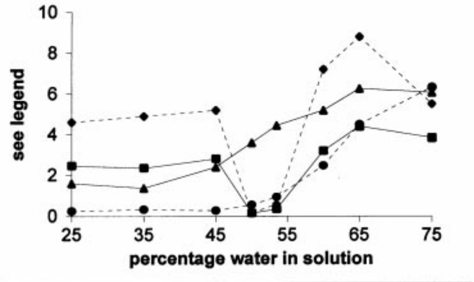

Fig. 5 Initial rates of reactions using various catalysts. The y-axis scales are as follows: reaction between material and benzaldehyde (**1**)—0.1 × % conversion after 10 minutes; reaction between **1** and **4**—0.1 × % conversion after 10 minutes; reaction between **2** and **4**—0.2 × % conversion after 15 minutes; reaction between **3** and **4**—0.25 × % conversion after 1 hour.

pore diameter, since the rate begins to increase even in samples before textural porosity is present. The trend for benzaldehyde **1** is, however, quite different. The rate appears to follow the same trend as for the cyclohexanone, with the exception of the two materials with irregular morphologies, AMP–HMS–53.5W and AMP–HMS–50W, where the activity is extremely low. The reaction with 3-pentanone **3** is, however, very different. In this case (the most difficult and slowest reaction), the rate of conversion correlates very well with changes in *textural porosity* rather than framework pore diameter. This echoes previous work, where the presence or absence of textural porosity has been cited as the predominant influence on the outcome of reactions.[35–40,58–60]

Stoichiometric reaction with benzaldehyde

This reaction follows the same trend as the catalytic reactions involving benzaldehyde, with a general trend towards higher activity with larger framework pore size, again with the exception of the two materials AMP–HMS–50W and AMP–HMS–53.5W. Both of these are extremely sluggish, although it is possible to achieve complete conversion of the amines to imines after 5–6 days of reaction (compare with 5–20 minutes for the other materials). A similar lack of stoichiometric activity has also been noted in other reactions of these two materials (*e.g.* alkylation), indicating an almost complete lack of nucleophilicity, despite their distinct basicity.[61]

Discussion

Changing the reaction medium in the preparation of aminopropyl hexagonal mesoporous silicas has a variety of effects. At the level of chemical composition, there is little significant change and certainly no trends are apparent. Furthermore, it appears that the templating mechanism holds over the range of solvents studied, although those prepared in high water content solvents appear to have slightly broader adsorption steps than those in the ethanol-rich domain. However, in the very water-rich region, the porosity is essentially textural. The incorporation of aminopropyl silane into the structure appears to be quantitative, as has been previously reported.[24] Interestingly, the amount of residual ethoxy groups remains constant over the range of solvent compositions studied. While it might be imagined that increasing the amount of water might increase the degree of hydrolysis, leading to lower amounts of residual ethoxy groups, this is not the case. We are currently investigating the effect of template removal using solvents other than ethanol to determine if this may cause some equilibration of the ethoxy content of the materials, but it is unlikely that complete scrambling would occur without the materials undergoing significant structural reorganisation and damage. Recently, it was disclosed that the use of aqueous acid can be used to remove template[62] thus avoiding the incorporation of ethoxy groups during template extraction. This was not used in this case, as the amine groups would become protonated during this process. It is unlikely that the amines could be liberated subsequently without considerable damage to the structure of the material. The similarity in the trends for both framework porosity and textural porosity between the extracted materials described here and those in which the template was removed by calcination[34] also suggests that significant structural damage does not occur during ethanol extraction. These similarities indicate that the action of the template in the synthesis is similar to that observed with all-silica HMS materials.[33,34,41] Thus the framework pore diameter is determined by increasing quantities of ethanol being incorporated into the head group layer of the micelle, causing contraction of the micelle, and leading to lower pore diameters with increasing amounts of ethanol. The textural characteristics follow the same trend indicated in previous work[34] and again, this indicates that similar template–silica(te) interactions are at play.

Two major differences are however seen—the particle size and morphology differ significantly, as does the chemical reactivity. The particles formed appear, by SEM, to be typical of HMS materials[22,33] for the majority of samples (AMP–HMS–25W, –30W, –35W, –40W, –45W, –60W, –65W, –75W) in that they are regular spheroidal particles intergrown to different extents. Within this group of materials, one major difference is evident. While the HMS materials of Pinnavaia[33,34] increase particle size significantly as the amount of ethanol increases (steadily by around an order of magnitude over a very similar range of solvent compositions), and the MCM-41 materials prepared by Di Renzo show a similar trend[41] on changing reaction medium, the materials prepared here have a constant particle size over the range of solvents investigated. The two previous articles mentioned, as well as others[63,64] are consistent with the particle size being controlled by classical crystallisation parameters, *i.e.* nucleation rate and growth rate. A fast nucleation rate favours small particles, due to the rapid formation of a large number of nuclei, leading to a short growth phase, and to a large number of small particles. Such a rapid nucleation process would be preferred in solvent mixtures rich in water, leading to more rapid hydrolysis and a larger number of nuclei. The expected dependence on mass transport to the growing interface is also observed—larger spheres are found in static conditions.[63] Thus, in the case of aminopropyl–HMS materials, the controlling parameters of particle growth appear to be different, despite the similarity in morphology. It may be that the presence of the aminopropylsilane causes an acceleration of the crystal growth process due to amine-catalysis of the hydrolysis and siloxane bond-forming processes[65,66] or that the presence of the amine causes a more rapid equilibration in hydrolysis/siloxane formation and subsequent nucleus formation and crystal growth. This would make the particle size thermodynamically controlled, perhaps leading to a more constant particle size. However, in a system already rich in amine (template) this appears unlikely. Nonetheless, it has been observed that, in all these systems, solid is formed very rapidly (within a few seconds), but the material subsequently appears to thicken very gradually over several hours after this initial appearance of solid. The effects of stirring in these systems are difficult to quantify, as the complex nature of the evolving system in terms of heterogeneity and changes in viscosity and thus mass transport will make a systematic study of these variables difficult. However, it may be that a combination of different factors are at play in a way which evens out conflicting effects, leading to a constant particle size.

The exceptions to this trend are the materials AMP–HMS–50W and AMP–HMS–53.5W. Both of these samples, prepared in the most water-rich of the *homogeneous* systems studied are more complex morphologically than the others. In addition to the usual spherical particles found in all the samples (which are the same size as found in the others) there are a large number of much larger and irregular particles, as well as some amorphous clusters of very small particles.

Thus the controlling factors of particle size and morphology are not clear in the AMP–HMS system. Nonetheless, it is clear that they are different to those which operate in the case of HMS and MCM-41 syntheses.

The chemical reactivity of aminopropyl groups grafted onto silica and HMS materials is typical of a primary amine. Thus, in addition to the expected ability to take part in base-catalysed reactions,[24,50,67–69] they can be alkylated by *e.g.* tosylates[70] and form imines very rapidly indeed with aldehydes.[44–46] The original AMP–HMS material prepared and evaluated as a base catalyst (AMP–HMS–53.5W) in the Knoevenagel reaction had catalytic activity similar to the corresponding AMP–silica material, but had a significantly higher catalytic lifetime, and a different poisoning mechanism. Intriguingly, this HMS material appears to have similar basicity to the silica-based material, but almost completely lacks nucleophilicity. In order to understand the nature of the amine groups in these materials we have investigated the reaction of the materials with benzaldehyde to form the corresponding imine (Figs. 3 and 4). Remarkably, the two materials which have irregularly shaped particles (AMP–HMS–50W and AMP–HMS–53.5W) display very low reactivity towards benzaldehyde. Otherwise, the activity of the materials follows the change in framework pore size, with larger pore size materials allowing faster reaction. Thus, diffusion plays a role in determining the rate of reaction of the aldehyde with the nitrogen. This reaction is very rapid with AMP–silica, and is complete in a few seconds. Only in the smallest pore material does the reaction stop short of completion, possibly due to pore blockage reducing diffusion rates even further. Interestingly, the dependence of catalytic activity on physical factors depends on the reaction studied. In the Knoevenagel reaction with benzaldehyde and ethyl cyanoacetate (complete in *ca.* 5 minutes with AMP–silica), the same trend is followed, the reaction becoming more rapid as the framework pore diameter increases, with the exception of the two "anomalous" materials, where reaction is very slow. However, in the reaction of ethyl cyanoacetate and cyclohexanone, the rate of reaction follows (roughly) the trend in framework pore size, but without the dramatic reduction in activity for the two irregular materials. These results indicate that, on these two materials, either the adsorption of benzaldehyde (but not ketones) occurs on a different part of the surface, away from the active sites, and that subsequent diffusion is slow, or adsorption is somehow disfavoured, or that the active site in the irregular materials is different to the active site in the other materials. Puzzlingly, this behaviour correlates with the morphology of the particles, but not with either chemical composition or with mesoscale parameters such as framework or textural porosity. Thus it appears that the factors which cause a change in the macroscopic (micron-scale) properties also cause a change in the surface chemistry, with concomitant effects on the reactivity and activity of the materials. A detailed spectroscopic investigation is underway to investigate these phenomena and the nature of the surface formed in different solvent systems, the results of which will be published in due course. Even more remarkably, the reaction of ethyl cyanoacetate with 3-pentanone, significantly more difficult than the reaction with cyclohexanone, displays a completely different behaviour. In this case, the controlling factor is clearly the textural porosity. This parameter has often been cited as a determining factor in the accessibility of materials to the framework pores,[34–40] and has often been invoked as being one of the most important structural features of an active catalyst. It is clear from the above results that this is not always the case, with the reaction of some substrates being influenced by textural factors, while others are dependent on framework porosity, and some on as yet undefined surface chemistry changes. Clearly, great care must be taken in the interpretation of structural effects on the rates of catalytic processes.

Conclusions

The preparation of AMP–HMS materials can be successfully carried out in a variety of solvent systems by varying the water : ethanol ratio. Particle size is independent of solvent composition, indicating that the formation of these materials does not follow the same trends as for the all-silica HMS materials already studied. Particles formed at the most water-rich of the homogeneous solvent compositions are very different and more complex morphologically. The framework pore diameter increases with increasing water content of the solvent, as does the framework pore volume. The textural porosity is negligible in homogeneous solvent systems, but as soon as the water content becomes high enough to make the template insoluble, the textural pore volume increases dramatically. This is consistent with previous work on all-silica HMS materials. The influence of structural features on chemical activity and reactivity depends on substrate—in reactions involving benzaldehyde or cyclohexanone with ethyl cyanoacetate, the catalytic activity of the materials increases with increasing framework pore diameter, and does not correlate with textural porosity, in contradiction to other studies. The reaction of benzaldehyde is complicated somewhat by the remarkable inactivity of the materials prepared with approximately equal weights of ethanol and water. The stoichiometric reaction of benzaldehyde with the amine to form the imine follows the same trend. This irregularity is also manifest in the particle morphology, indicating that both the surface chemistry and the formation of particles are different in these solvent systems, and that both these anomalous behaviours may be related to the same primary phenomenon. The activity of the materials discussed here is thus a function of surface chemistry, particle morphology (or the factors controlling the morphology), the framework pore size *and* the textural properties of the materials. The relative importance of these parameters is also substrate dependent. This represents an important *caveat* in the interpretation of changes in rate and conversion in reactions involving such materials, since the nature of the material is influenced by solvent composition (and potentially by many other preparative variables) in many ways.

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