The use of acidic task-specific ionic liquids in the formation of high surface area mesoporous silica

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The acidic ionic liquids 1-alkyl-3-methylimidazolium hydrogen sulfate [C_nMIM]HSO_4 (n = 8, 10, 12, 16) were synthesised using a one-pot method and then used as new acidic templates to generate high surface area ordered mesoporous silicas (>1000 m^2 g^{-1}) using a one-step synthetic route.

The discovery of three-dimensional ordered mesoporous silica[1] has generated wide interest in the synthesis of mesoporous materials based on self-assembly of ordered, surfactant/inorganic structures. Routes based on ionic, hydrogen and covalent bonding between the surfactant and the inorganic precursors have been developed for the synthesis of mesoporous silicas and other metal oxides. Much effort has been focused on developing ordered periodic mesoporous materials with well-defined, controlled pore channels by sol–gel templating using amphiphilic surfactants as templates.[2,3]

Room temperature ionic liquids (RTILs) have attracted much attention due to their unusual properties, especially their low vapour pressure, high thermal and chemical stability, and excellent solvating power for organic and inorganic compounds.[4–6] Since most long-chain RTILs possess both a hydrophilic ionic head group and a hydrophobic organic chain, they represent a category of surfactant and can form liquid crystals in various solvents. Accordingly, they can be used as templates to prepare microporous and mesoporous materials.[7,8] In addition, they have been widely utilised as environmentally benign solvents for various processes, including synthesis, separation and catalysis, frequently achieving higher catalytic activity and/or selectivity than accessible with traditional solvents.[9,10] They are also a novel class of salts that have already been found to perform well in the preparation of nanostructured materials and nanoparticles for catalysis.[11,12]

Seddon *et al.*[13] and other groups have been interested in using ionic liquids as reaction media for synthesising advanced materials. Herein, we report the dual use of a range of acidic ionic liquids in which the cation acts as a template and the anion as the acid source for the synthesis of mesostructured hybrid silica materials.

As the name suggests, task-specific ionic liquids (TSILs) perform a dual role in a process for which they are being applied. Often, these dual roles are claimed to be as a solvent and as a catalyst for the reaction being performed. The most obvious cases involve the use of acidic ionic liquids (usually possessing the HSO_4^- anion) catalysing various reactions such as the Biginelli reaction,[14] Friedel–Crafts alkylation,[15] hydrolytic reactions,[16] and electrophilic substitution.[17]

Herein we describe the one-pot microwave synthesis of the acidic ionic liquids 1-alkyl-3-methylimidazolium hydrogen sulfate (where alkyl = octyl, decyl, dodecyl, hexadecyl) and their subsequent application as both templates and acid source for the synthesis of (short-range) ordered, high-surface-area mesoporous silicas.

The acidic ILs [C_nMIM]HSO_4 (n = 8 (**1**), 10 (**2**), 12 (**3**), 16 (**4**)) were synthesised by a one-pot method using microwave irradiation and obtained as a viscous orange oil in the case of **1** and white waxy solids for **2–4**. The method involved microwave irradiation of equimolar quantities of 1-methylimidazole, the appropriate alkyl halide and $NaHSO_4$. The counterion was added to the synthesis in three approximately equal aliquots to allow for complete reaction to occur during the irradiation process. With the counterion being present in the reaction mixture, the high temperature of the reaction and the solubilising power of the ILs allow for the anion exchange to occur *in situ*, rather than post-synthetically. Post-synthetic anion exchange can be difficult due to the low solubility of salts such as $NaHSO_4$ in organic solvents. Once the crude reaction mixture had cooled, the product was extracted with CH_2Cl_2 and filtered to remove unwanted salts (NaBr and unreacted $NaHSO_4$). Upon removal of the solvent *in vacuo*, the product was washed with hexane and diethyl ether to afford the products as viscous oils or white solids. The overall yields of **1–4** were greater than 80% after purification. Products **1–4** were characterised by ^{1}H and ^{13}C{^{1}H} NMR. Testing of the ILs for halides using silver nitrate revealed the presence of trace amounts of halides in the final products. This, however, does not affect their usefulness as templates or as hydrolysis catalysts for the preparation of mesoporous silicas.

The basic molecular structure of the new ionic liquids is shown in Fig. 1. The head group of these new templates is the alkylated imidazolium cation, which can interact not only with negatively charged silica precursors but also potentially with the hydrophobic organic bridges of silsesquioxanes.[18] Cetyltetrabutylammonium bromide (CTAB), a frequently used template for the preparation of mesostructured materials,[2,19] requires the addition of an acid or base to catalyse the hydrolysis of the silica precursor and subsequent

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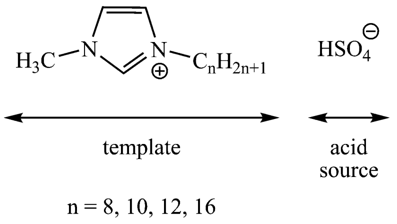

Fig. 1 Dual characteristics of the acidic ionic liquids.

silica-forming condensation reactions. Thus, these new ILs, when used in the preparation of mesoporous silicas, serve the dual roles of template and acid source.

The mesoporous silicas were prepared by a hydrothermal synthesis procedure using tetraethyl orthosilicate (TEOS) as the silica source and task specific ionic liquids (TSILs) as the structure directing agent and acid source. The final product was ground into powder for further characterisation. The surface areas, pore sizes, and pore volume of mesostructured materials obtained when the acidic ionic liquids are used as templates are summarised in Table 1. The materials generated show an increase in surface area with increase in the alkyl chain length of the ionic liquid to a maximum of 1103 $m^2\ g^{-1}$ when $[C_{16}MIM]HSO_4$ is used as the template. The pore sizes show a significant decrease from 99 Å to 41 Å with an increase in chain length from 8 to 16. The large difference in pore sizes associated with the C-8 chain length *versus* the C-10 and higher is consistent with a different, *i.e.* non-micellar, templating mechanism for C-8 (*e.g.* similar to that ascribed to the TUD-1 structure family).[20] The decrease in pore size going from C-10 to C-11 can be attributed to the more efficient packing of the longer alkyl chains.

The XRD patterns of the mesostructured materials are shown in Fig. 2. These patterns correspond closely to the structured mesoporous materials reported by Kresge *et al.*,[19] Zhou *et al.*[21] and Stucky *et al.*[3] Miskolczy *et al.*[22] reported that as the alkyl chain length of the template increased, the materials showed improved X-ray diffraction patterns. The same group also reported that ionic liquids should have at least nine carbon atoms in their hydrophobic tail to form micelles in aqueous solution which suggests that in the case of the template with the C_8 alkyl chain (**1**) it would be very difficult to form a structured mesoporous material. This hypothesis matches with the data presented in Fig. 2. In the case of **I**, the XRD pattern does not have the (100) reflection present in silicas **II**, **III** and **IV** indicating that this silica does not possess any regular repeating structure. The presence of the peak at $\sim 3^\circ\ 2\theta$ indicates that the pore sizes in the silicas **II**, **III** and **IV** have a narrow pore size distribution which gives rise to regions of short-range order. The lack of long-range order is indicated by the absence of additional reflections in the XRD patterns.

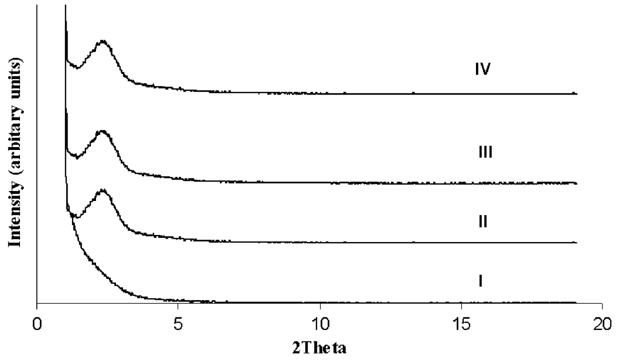

Fig. 2 X-Ray diffraction patterns of silicas **I–IV**.

The TEM images reveal that none of the siliceous materials prepared by this method have any observable long-range order. The images of **I** and **IV** (Fig. 3) show that the silicas have a sponge-like topology. This observation is consistent with the XRD data.

The nitrogen adsorption–desorption isotherms for each of the silicas **I**, **II**, **III** and **IV** are classic Type IV curves which indicates that the silica is mesoporous in nature (Fig. 4), as such materials have pore sizes in the range of 2–50 nm and are characterised by Type IV isotherms which have a hysteresis. This type of isotherm indicates that capillary condensation is occurring during the adsorption process. These results are similar to Zhou's work on ionic-liquid-casted supermicroporous lamellar phase silica,[21] which shows that imidazolium-based ionic liquids can template ordered mesoporous silica as well as supermicroporous lamellar silica.

We have demonstrated a self-assembly synthesis of mesoporous materials using acidic ILs. This research clearly opens an easy method of synthesis of mesoporous materials using acidic ILs.

Experimental

Microwave irradiations were performed using a Milestone BatchSYNTH in a 2-necked round-bottom flask fitted with a reflux condenser. ^1H NMR (300.13 MHz) spectra and $^{13}C\{^1H\}$ NMR (75.48 MHz) spectra were recorded using a Bruker DPX300 NMR spectrometer and were referenced internally to residual proteo-solvent impurities (CD_3CN, δ 1.94 (^1H NMR) and δ 1.32 (^{13}C NMR)). Mass spectra (ESI) were recorded on a Finnigan LCQ MS detector. X-ray diffraction patterns were recorded using a Siemens D5000 diffractometer using CuKα radiation at 40 kV. Diffraction patterns were recorded in the 1–60° 2θ range in steps of 0.02 s with 15 s per step. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics ASAP2020 surface area and porosity analyser

Table 1 The surface area, pore sizes and pore volumes of the mesostructured silicas **I–IV**

Silica	TSIL	Surface area/$m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$	Pore size/Å
I	$[C_8MIM]HSO_4$	737	1.820	98.85
II	$[C_{10}MIM]HSO_4$	991	1.475	59.54
III	$[C_{12}MIM]HSO_4$	1017	1.149	45.19
IV	$[C_{16}MIM]HSO_4$	1103	1.020	41.22

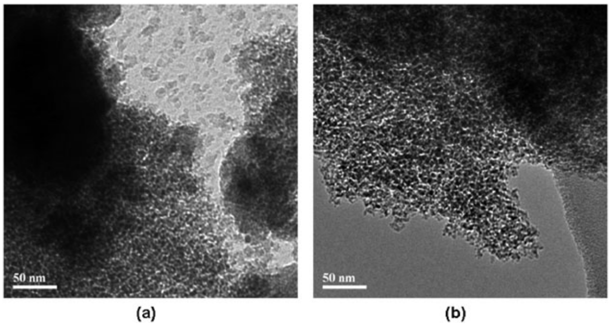

Fig. 3 TEM images of silica **I** (a) and **IV** (b).

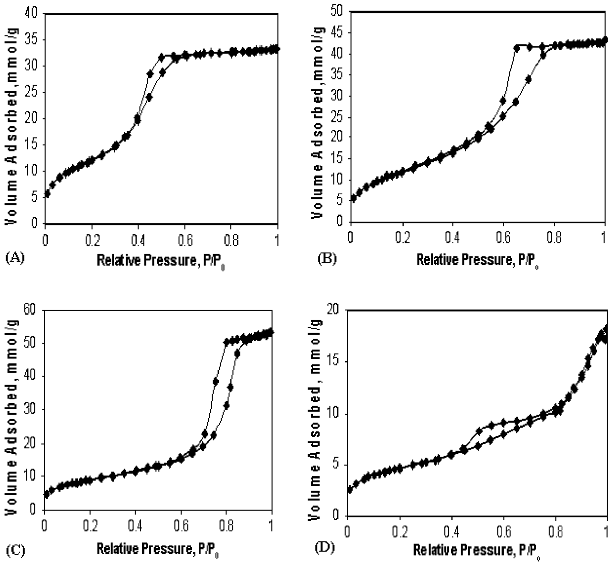

Fig. 4 Nitrogen adsorption–desorption isotherms recorded at 77 K for silicas **I** (A), **II** (B), **III** (C), and **IV** (D).

using ∼100 mg of the siliceous material. The data were obtained by liquid nitrogen adsorption and desorption at various nitrogen partial pressures and were analysed by the BJH (Barrett–Joyner–Halenda) and the BET (Brunauer–Emmett–Teller) methods. The pore size distribution curve was derived from the analysis of the adsorption branch of the isotherm. Transmission electron micrographs were recorded digitally with a Gtan slow-scan charge-coupled device (CCD) using a Phillips CM120 Biotwin electron microscope operating at 120 kV. The samples were prepared by dispersing the powder products as a slurry in ethanol, which was then deposited and dried on a holey carbon film on a Cu grid.

Synthesis of acidic ionic liquids

A typical synthesis involved mixing a 1.05 molar excess of 1-alkyl bromide (60.9 mmol) to 1-methylimidazole (4.76 g, 58.0 mmol). To this mixture was added NaHSO$_4$ (∼2.0 g). The mixture was then irradiated in a microwave for 5 min at 300 W to a maximum temperature of 110 °C. After this time additional NaHSO$_4$ (∼2.0 g) was added and irradiated again. This procedure was repeated until a molar equivalent of NaHSO$_4$ (7.32 g, 60.9 mmol) had been added. After the final addition, the reaction mixture was irradiated for 12 min at 300 W at 110 °C. The product was extracted with CH$_2$Cl$_2$ (100 mL) and filtered to remove the salts. The solvent was removed *in vacuo*. The resultant oil was washed with diethyl ether (2 × 100 mL). The product was then dried *in vacuo* at 80 °C to afford the product.

1-Methyl-3-octylimidazolium hydrogen sulfate 1. ^{1}H NMR (CD$_3$CN): δ 9.97 (s, ImC$_2$-H), 7.60 (m, 1H, ImH), 7.44 (m, 1H, ImH), 4.24 (t, 2H, $^3J_{HH}$ = 7 Hz, N-CH$_2$), 4.04 (s, 3H, N-CH$_3$), 1.84 (m, 2H, NCH$_2$CH$_2$), 1.21 (m, 10H), 0.76 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$) ppm. ^{13}C {^{1}H}NMR (CD$_3$CN): δ 137.17, 123.78, 122.03, 67.73, 50.02, 36.60, 31.57, 30.21, 28.92, 28.85, 26.15, 22.46, 13.95 ppm. *m*/*z* (ESI+): 195 (*M*+, 100%).

1-Methyl-3-decylimidazolium hydrogen sulfate 2. ^{1}H NMR (CD$_3$CN): δ 9.22 (s, ImC$_2$-H), 7.51 (m, 1H, ImH), 7.48 (m, 1H, ImH), 4.19 (t, 2H, $^3J_{HH}$ = 7 Hz, N-CH$_2$), 3.89 (s, 3H, N-CH$_3$), 1.82 (m, 2H, NCH$_2$CH$_2$), 1.24 (m, 16H), 0.85 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$) ppm. ^{13}C {^{1}H}NMR (CD$_3$CN): δ 137.60, 124.47, 123.92, 50.32, 32.55, 30.66, 30.27, 30.18, 30.05, 29.93, 29.60, 26.65, 23.30, 14.35 ppm. *m*/*z* (ESI+): 223 (*M*+, 30%).

1-Methyl-3-dodecylimidazolium hydrogen sulfate 3. ^{1}H NMR (CD$_3$CN): δ 9.18 (s, ImC$_2$-H), 7.49 (m, 1H, ImH), 7.46 (m, 1H, ImH), 4.18 (t, 2H, $^3J_{HH}$ = 7 Hz, N-CH$_2$), 3.88 (s, 3H, N-CH$_3$), 1.82 (m, 2H, NCH$_2$CH$_2$), 1.25 (m, 18H), 0.86 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$) ppm. ^{13}C {^{1}H}NMR (CD$_3$CN): δ 137.03, 123.96, 122.62, 66.90, 50.95, 36.30, 32.06, 30.15, 29.78 (2 carbons), 29.69, 29.56, 29.50, 29.10, 26.15, 22.81 ppm. *m*/*z* (ESI+): 251 (*M*+, 100%).

1-Methyl-3-hexadecylimidazolium hydrogen sulfate 4. ^{1}H NMR (CD$_3$CN): δ 9.12 (s, ImC$_2$-H), 7.47 (m, 1H, ImH), 7.44 (m, 1H, ImH), 4.18 (t, 2H, $^3J_{HH}$ = 7 Hz, N-CH$_2$), 3.88 (s, 3H, N-CH$_3$), 1.82 (m, 2H, NCH$_2$CH$_2$), 1.26 (m, 26H), 0.87 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 137.46, 124.28, 123.14, 68.69, 50.36, 36.81, 32.56, 30.63, 30.27 (4 carbons), 30.18, 30.05, 29.99, 29.58, 26.64, 23.31, 14.33 ppm. *m*/*z* (ESI+): 307 (*M*+, 100%).

Synthesis of mesoporous silica templated with acidic ionic liquids

In a typical synthesis [C$_n$MIM]HSO$_4$ (1.0 g, 3.42 mmol) and tetraethoxysilane (TEOS, 0.71 g, 3.42 mmol) were dissolved in ethanol under mild magnetic stirring. After homogenisation of the mixture, water (0.68 g, 37.6 mmol) was added dropwise and the mixture stirred until a homogenous gel was obtained. The molar compositions of the starting mixtures were 1 TEOS : 1 [C$_n$MIM]HSO$_4$: 11 H$_2$O. The resulting mixtures were then transferred to a PTFE-lined steel autoclave and heated at 160 °C for 118 h. After hydrothermal treatment, the mixtures were dried at 190 °C for 124 h and then calcined at 550 °C for 110 h with a temperature ramp rate of 165 °C min^{-1} under a stream of air to remove the template.

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