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The influence of template extraction on the properties of primary amine templated aluminosilicate mesoporous molecular sieves

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Aluminosilicate mesoporous molecular sieves (Al-MMS) prepared at room temperature using hexadecylamine as template have been subjected to template extraction prior to calcination. Extraction in ethanol alone removes only that part of the template (in neutral form) which is not associated with framework Al while the presence of a cation (Na^+ or NH_4^+) ensures total template removal. Template extraction has no effect on elemental composition and for dry (non-calcined) samples results in an improvement in structural ordering. The effect of calcination depends on the mode of extraction; samples extracted in ethanol or ethanol/NH_4^+ are structurally stable to calcination and possess surface area and pore volume similar to directly calcined samples while ethanol/Na^+ extracted samples are relatively unstable and undergo considerable structural degradation resulting in lower surface area and pore volume. Dealumination results from calcination of amine or ammonium ion containing samples while Na containing samples do not undergo any dealumination. The acid content of calcined ethanol and ethanol/NH_4^+ extracted samples is comparable to that of the directly calcined samples but the extracted samples exhibit higher catalytic activity for the cracking of cumene. Calcined ethanol/Na extracted samples possess very low acidity and exhibit no catalytic activity.

Introduction

Recent advances in the synthesis of mesoporous molecular sieves which possess uniform and sharply distributed pores of diameter 20–100 Å have increased the range of well ordered solid acid catalysts (previously the domain of microporous zeolites) into the mesoporous regime.[1] Synthesis of such silica based materials involves the use of surfactants to assemble inorganic species from solution into a solid framework in which the organic surfactant template is occluded.[2–4] The removal of the template to generate the molecular sieve with regular void spaces is therefore an integral part of the synthetic process. For M41S materials which are synthesised using a cationic surfactant and anionic inorganic species, template removal may be achieved either by calcination or by solvent extraction followed by calcination.[5,6] It has been shown that more of the template is removed during the extraction if the solvent system contains a cation donor such as an acid or salt.[5–7] For Al-containing MCM-41, template removal by solvent extraction results in an increase in the amount of non-framework octahedral Al (due to partial dealumination). Furthermore solvent extraction on its own does not readily remove any template associated with tetrahedrally coordinated framework Al and therefore calcination at elevated temperature is required to ensure complete removal of the template.[7] Tanev and Pinnavaia[8] have, however, shown that in the absence of strong electrostatic interactions between the surfactant and framework (*e.g.* when neutral primary amine micelles are used to direct the assembly of neutral silica inorganic species) it is possible to achieve complete template removal by solvent extraction alone.

We have recently reported the synthesis, acidity and catalytic properties of Al-containing mesoporous molecular sieves (Al-MMS) prepared using primary amines as the templates.[9–11] We have shown that when compared to equivalent Al-containing MCM-41 materials the Al-MMS materials possess significantly higher Brønsted acid content and consequently exhibit higher catalytic activity for Brønsted acid catalysed reactions such as the cracking of cumene.[10,11] In the synthesis of Al-MMS materials the primary amine surfactant micelles act both as structure directing agents during the assembly of soluble silicon/aluminium species and also as a source of charge balancing protons (during calcination of the as-synthesised material). This is advantageous because Brønsted acid sites are generated by simple calcination. We and others have shown that in contrast to the purely siliceous analogue, where all the amine is in neutral form, a part of the templating amine in the Al-MMS samples exists in a protonated form where it is electrostatically bound to the inorganic framework and cannot therefore be removed by simple solvent extraction.[9,12] The proportion of such protonated amine increases with the amount of aluminium in the solid framework.[9] We also found that high amounts of aluminium in the Al-MMS framework increased the attraction between the templating amine micelles and the framework and thus removal of the template by direct calcination resulted in greater structural (framework) collapse due to the increase in local heating effects.[11] It is thus of interest to investigate other methods of template removal. Here we report a detailed comparison of the properties of Al-MMS catalysts prepared at room temperature using hexadecylamine as template and subjected to various methods of template removal. Directly calcined samples are compared with samples in which template removal is achieved by extraction using ethanol alone followed by calcination or by solvent extraction using ethanol in the presence of an acid generating (NH_4^+) or a non-acidic (Na^+) cation prior to calcination. We have investigated the effects of the extraction procedure on the structural integrity of the Al-MMS materials and also on the nature of the Al they contain. We also report on the influence of the template extraction procedure on the acidity and catalytic performance for cumene cracking. Particular emphasis is given to the effect of cations during the extraction.

Experimental

Synthesis of materials

The as-synthesised aluminosilicate materials were prepared as follows: aluminium isopropoxide [$Al(i\text{-}C_3H_7O)_3$ dissolved in 35 ml isopropanol] was mixed with 0.2 mol tetraethylorthosilicate

(TEOS, in 80 ml ethanol) at Si/Al molar ratios in the range 40–5/1 and vigorously stirred at room temperature for 15 minutes. The template solution was separately prepared by dissolving 0.05 mol hexadecylamine in a mixture of 80 ml water and 120 ml ethanol. The TEOS–Al(i-C_3H_7O)$_3$ mixture was added to the template solution under vigorous stirring at room temperature. The pH of the synthetic mixtures was close to 9.5. The resulting gel mixture was allowed to react at room temperature for 20 hours following which the solid product was obtained by filtration and air dried at room temperature. Template removal was achieved either by direct calcination in air at 650 °C for 4 hours or by solvent extraction prior to calcination. Solvent extraction was performed as follows: 1.5 g of the dry (as synthesised) material was added to 150 ml of extraction media and stirred at 65 °C for 1 h followed by filtration and washing with ethanol. This procedure was repeated once to give the 'dry extracted' samples. Three types of extraction media were used: (1) 150 ml ethanol alone; (2) 1.5 g of sodium acetate in 150 ml ethanol; and (3) 1.5 g ammonium acetate in 150 ml ethanol. All the 'dry extracted' samples were then calcined in air at 650 °C for 4 hours. The directly calcined materials are designated Al-MMSX (where X is the Si/Al ratio used in the synthesis gel). The extracted samples are named with a prefix indicating the extraction media (Et for ethanol alone; NH for ammonium acetate and Na for sodium acetate)

Characterisation

Elemental composition (*via* EDA analysis) was obtained using a Camscan S4 scanning electron microscope at 20 kV. The data were processed through a ZAF4 program running on a Link 860 series 2 processor. TGA and DTG curves were obtained using a Polymer Laboratories TG analyser with a heating rate of 20 °C min^{-1} under nitrogen flow of 25 ml min^{-1}. Powder X-ray diffraction (XRD) patterns were recorded using a Philips 1710 powder diffractometer with Cu-Kα radiation (40 kV, 40 mA), 0.02° step size and 1 s step time. Textural properties (surface area, pore volume and pore size) were determined at −196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP 2400 sorptometer. Before measurement each sample was oven dried at 280 °C and evacuated overnight at 200 °C under vacuum. ^{27}Al magic-angle-spinning (MAS) NMR spectra were recorded at 9.4 T using a Chemagnetics CMX-400 spectrometer with zirconia rotors 4 mm in diameter spun at 8 kHz. The spectra were measured at 104.3 MHz with 0.3 s recycle delays and corrected by subtracting the spectrum of the empty MAS rotor. External $Al(H_2O)_6^{3+}$ was used as a reference. To ensure quantitative reliability all calcined samples were fully hydrated and equilibrated with room air prior to the measurements.[13]

Acidity measurements

The acid content of the materials was measured by using TPD of cyclohexylamine. The samples were exposed to liquid cyclohexylamine at room temperature after which they were kept overnight (at room temperature) and then in an oven at 80 °C for 2 hours so as to allow the base to permeate the samples. The oven temperature was then raised to 250 °C and maintained at that temperature for a further 2 hours. The samples were then cooled to room temperature under dry nitrogen following which they were subjected to thermogravimetric analysis using a Polymer Laboratories TG analyser with a heating rate of 20 °C min^{-1} under nitrogen flow of 25 ml min^{-1}. The weight loss associated with desorption of the base from acid sites occurred between 300 and 450 °C, with a maximum at *ca.* 370 °C. This weight loss was used to quantify the acid content (in μmol of cyclohexylamine per gram of sample) assuming that each mole of cyclohexylamine corresponds to one mole of protons.[11,14]

Catalytic testing

The conversion of cumene was performed at 300 °C and a WHSV of 4.0 using a tubular stainless steel, continuous flow fixed-bed microreactor (of internal diameter 10 mm) with helium (25 ml min^{-1}) as carrier gas. The catalyst bed (100 mg; 30–60 mesh) was first activated for 1.5 h at 500 °C under helium (25 ml min^{-1}). For the reaction a stream of cumene vapour in helium was generated using a saturator at room temperature. The reaction products were separated and analysed using a Carlo Erba HRGC 5300 gas chromatograph on line with the microreactor. Gas chromatographs were obtained automatically on samples of the product stream which were collected at regular intervals using a Valco 6-port valve. The gas chromatographs were used to calculate the percent overall cumene conversion.

Results and discussion

Chemical composition and thermal analysis

The bulk Si/Al molar ratios of the parent (directly calcined) Al-MMS samples, shown in Table 1, indicate that Si and Al are incorporated into the solid framework in proportions which are largely in line with the synthesis gel composition. The mode of template extraction does not have any significant or systematic effect on the Si/Al ratio except that for samples derived from Al-MMS20 there is some preferential leaching of a small amount of silica (see Table 1) reflected in lower Si/Al ratios. However samples derived from Al-MMS10 (data not shown) had very similar Si/Al ratios (in the range 12.8 ± 0.3) which implies that silica leaching is not necessarily a characteristic of solvent mediated template extraction.

Fig. 1 shows the TGA and DTG curves obtained for the as-synthesised purely siliceous sample (prepared according to ref. 9) and the Al-MMS samples. The first mass loss between 25 and 100 °C is attributed to the release of water and/or ethanol. All samples show a further mass loss centred at *ca.* 300 °C which is due to amine desorption. In addition the Al-MMS samples show a third mass loss centred at 450 °C which increases as the (synthetic gel) Si/Al ratio reduces and develops at the expense of the mass loss centred at 300 °C. We have previously shown that for primary amine templated aluminosilicate samples such as those described here, the occluded amine exists in two forms, *i.e.*, neutral 'low temperature' amine similar to that present in the purely siliceous material and electrostatically bound 'high temperature' amine.[9] During thermogravimetric analysis the former less strongly bound template is desorbed and decomposed between 100 and 350 °C while the electrostatically bound template is removed between 350 and 500 °C. However, despite the varying amounts of neutral and charged amine, it is clear from Fig. 1 that the total amine occluded remains more or less the same regardless of the Si/Al ratio. This implies that both the neutral and charged amine are occluded in micellar arrangements which are encased by the inorganic framework. As more Al is incorporated into the framework more of the occluded amine is protonated so as to balance the resulting negative charge.

Fig. 2 compares the TGA and DTG curves of the dry parent (as-synthesised) Al-MMS10 sample before and after being subjected to various modes of template extraction. The mass loss between 150 and 800 °C, which excludes adsorbed water or ethanol, was 36% for the parent as-synthesised Al-MMS10 sample and 26, 11 and 10% for Et-, NH- and Na-Al-MMS10 samples respectively. Unlike the parent sample, the ethanol-extracted sample (Et-Al-MMS10) shows only one mass loss due to the desorption of electrostatically bound amine. Thus extraction in ethanol alone removes the neutral amine but has no noticeable effect on the electrostatically bound amine. On the other hand the TGA and DTG curves

Table 1 Elemental composition, *d* spacing and textural properties of calcined Al-MMS samples subjected to various modes of template removal

Sample	Si/Al ratio	d_{100}/Å	Surface area/ $m^2\ g^{-1}$	Pore volume/ $cm^3\ g^{-1}$	APD[a]/Å	a_0[b]/Å	Wall thickness/Å
Directly calcined							
Al-MMS40	44.1	35.1	1165	0.67	25.1	40.5	15.4
Al-MMS20	26.3	34.2 (35.8)[c]	1050	0.58	23.7	39.5	15.8
Al-MMS10	12.8	32.2	1104	0.47	21.2	37.2	16.0
Al-MMS5	7.6	31.6	901	0.40	20.1	36.5	16.4
Extracted prior to calcination							
Et-Al-MMS20	22.7	36.0 (37.0)[c]	941	0.81	26.4	41.6	15.2
NH-Al-MMS20	24.1	36.2 (38.4)[c]	894	0.71	25.7	41.8	16.1
Na-Al-MMS20	24.6	32.5 (36.0)[c]	731	0.53	27.8	37.5	9.7

[a] APD = Average pore diameter (determined using BJH analysis). [b] a_0 = Lattice parameter, from the XRD data using the formula $a_0 = 2d_{100}/\sqrt{3}$. [c] Values in parentheses are *d* spacing before calcination.

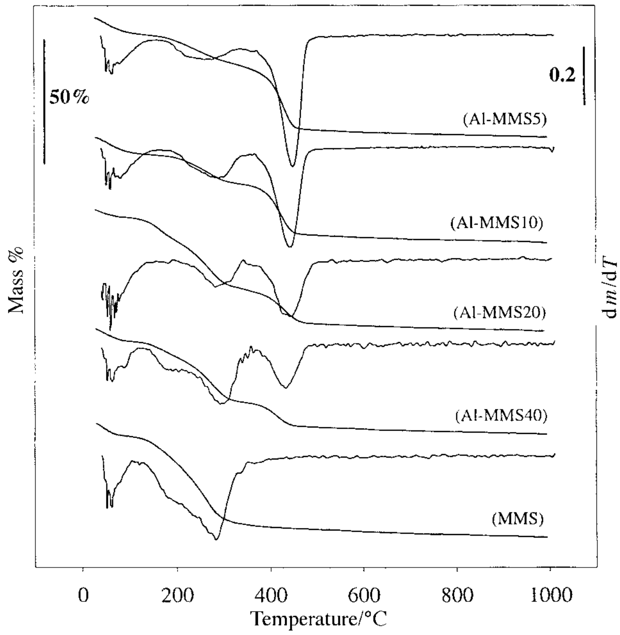

Fig. 1 Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis curves for as-synthesised purely siliceous (MMS) and Al-MMS samples.

of NH- and Na-Al-MMS10 indicate that extraction in the presence of a cation removes all the occluded amine. Indeed FTIR spectroscopy confirmed the total removal of amine from samples subjected to template extraction in the presence of NH_4^+ and Na^+ ions, *i.e.*, we did not observe any peaks attributable to hexadecylamine. This means that the events in the TGA curve of the NH- and Na-Al-MMS10 samples are new and are not attributable to amine desorption. For Na-Al-MMS10 we attribute the mass loss centred at *ca.* 550 °C to dehydroxylation. The dehydroxylation starts at 200 °C and is complete at 700 °C. The DTG of the NH-Al-MMS10 sample shows two mass losses in the temperature range 200–500 °C which we attribute to the decomposition of ammonium ions. The presence of two distinct mass losses suggests two types of ammonium ions, one more stable than the other. If we consider the NH-Al-MMS10 sample as being similar to an ammonia saturated solid Brønsted acid material, with the base adsorbed as ammonium ions on Brønsted acid sites, it is then possible to ascribe the mass loss centred at 350 °C to diamination from weaker acid sites while ammonium ions held on stronger acid sites are desorbed at the higher (420 °C) temperature. This explanation is supported by Fig. 3 which shows TGA and DTG curves of all the Al-MMS samples after template extraction in the presence of NH_4 ions. As the Si/Al reduces, the mass loss at 420 °C increases which is agreement with higher population of strong acid sites due to increasing Al incorporation.

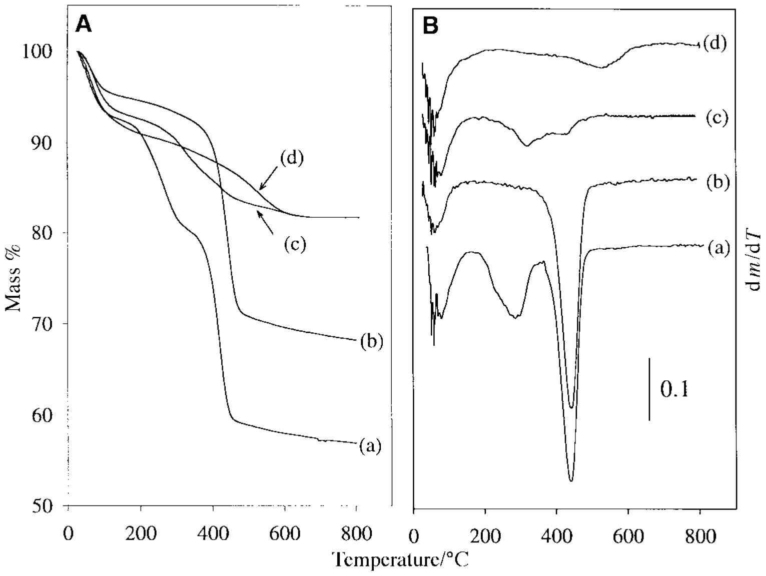

Fig. 2 (A) Thermogravimetric analysis (TGA) and (B) differential thermogravimetric (DTG) analysis curves for an Al-MMS sample prepared at Si/Al = 10 before and after template extraction; (a) as-synthesised, (b) extracted in ethanol alone, (c) extracted in ethanol/NH_4^+, (d) extracted in ethanol/Na^+.

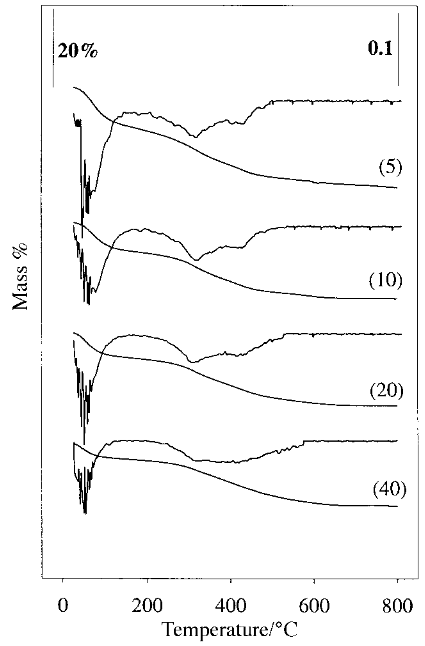

Fig. 3 Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis curves for Al-MMS samples after template extraction in ethanol/NH_4^+.

Physical characterisation

The XRD patterns of the as-synthesised and (directly) calcined parent Al-MMS materials are shown in Fig. 4. The samples mainly exhibit a single basal (100) peak which is characteristic of materials possessing short range hexagonal ordering.[8] As-synthesised materials prepared at Si/Al > 10 show an additional weak and diffuse peak at *ca.* 1.8 nm which may be an indication of slightly better long range ordering in these silica-rich materials. On calcination the scattering intensity of the basal peak increases. The increase in scattering intensity observed here may be due to better ordering of the inorganic framework (as a result template removal and formation of cross-linking siloxane bonds) or increase in scattering domain size. However despite the increase in the intensity of the basal peak (especially for Al-MMS40), the diffuse peak at *ca.* 1.8 nm disappears which again emphasises the absence of long range order. As expected for such mesoporous materials,[15] the intensity of the basal peak reduces with increase in Al incorporation indicating that Al has a deleterious effect on structural ordering. Furthermore as the amount of Al incorporated increases the *d* spacing reduces (see Table 1).

Fig. 5 compares the XRD patterns of the parent as-synthesised (dry) and calcined Al-MMS20 samples with equivalent samples after being subjected to template extraction (dry samples) and subsequent calcination. For the dry samples template extraction has the effect of increasing the intensity of the basal (100) peak. This may be related to better ordering occasioned by the benign removal of all or some of the template and formation of cross-linking siloxane or Si–OH–Al bonds. Upon calcination the intensity of the basal peak for Et-Al-MMS20 and NH-Al-MMS20 is maintained suggesting that structural ordering is retained in the calcined forms of these samples. For Na-Al-MMS20 the decrease in intensity of the basal peak is indicative of some structural collapse which in turn suggests that template free Na-containing Al-MMS materials are unstable towards calcination (see interpretation of porosity data). Similar behaviour has been previously reported for aluminosilicate Na-MCM-41 materials from which most of the template had been extracted.[7] The instability of template free Na-containing Al-MMS materials is further highlighted by the extent of lattice contraction due to calcination; the basal spacing of Na-Al-MMS20 reduces by 9.7% compared to 4.5, 2.7 and 5.7% for the parent (as-synthesised), Et-Al-MMS20 and NH-Al-MMS20 samples respectively (see Table 1). The higher contraction for Na-Al-MMS20 suggests extensive dehydroxylation which supports our interpretation of the TGA results described above. We note that calcined Et-Al-MMS20 and NH-Al-MMS20 samples have similar d_{100} spacings despite the larger lattice contraction in the latter.

The textural parameters of the parent (directly calcined) Al-MMS materials are given in Table 1 while Fig. 6 shows the corresponding nitrogen sorption isotherms. The isotherms exhibit a mesopore filling step in the relative pressure (p/p_o) range 0.05 to 0.4 which is characteristic of such materials.[16] The height and steepness of the step which are an indication of the extent and uniformity of the mesopores reduce at lower Si/Al ratios. This is due to increasing amount of framework

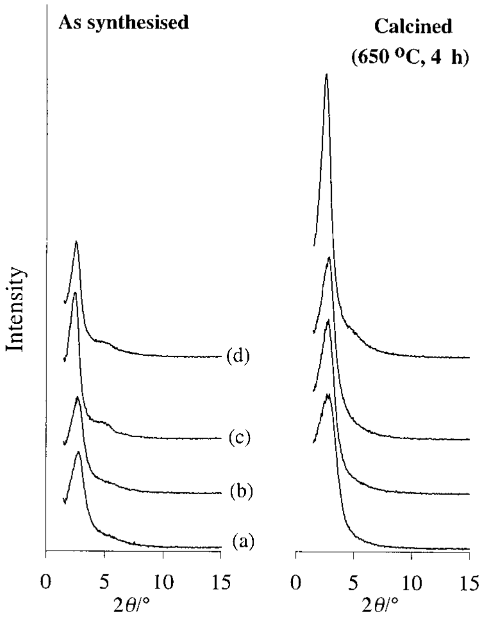

Fig. 4 Powder XRD patterns of as-synthesised and calcined Al-MMS samples prepared at Si/Al of (a) 5, (b) 10, (c) 20 and (d) 40.

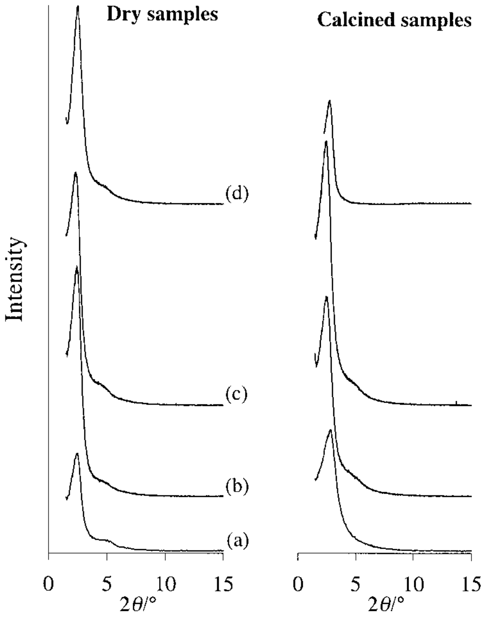

Fig. 5 Powder XRD patterns of dry and calcined Al-MMS samples prepared at Si/Al = 20; (a) as-synthesised, (b) extracted in ethanol alone, (c) extracted in ethanol/NH_4^+, (d) extracted in ethanol/Na^+.

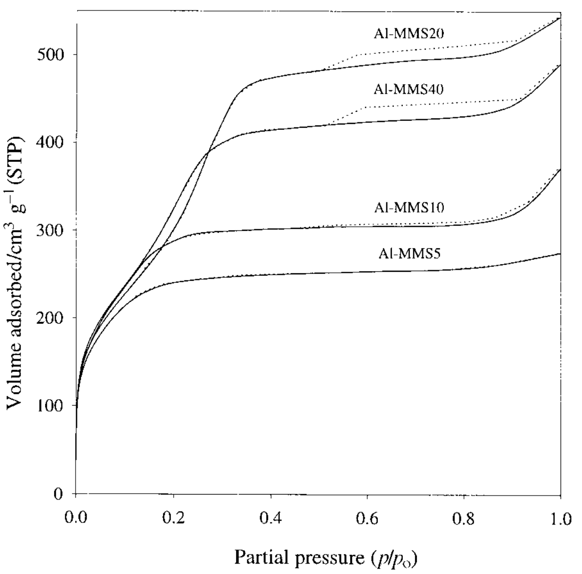

Fig. 6 Nitrogen sorption isotherms of directly calcined Al-MMS samples.

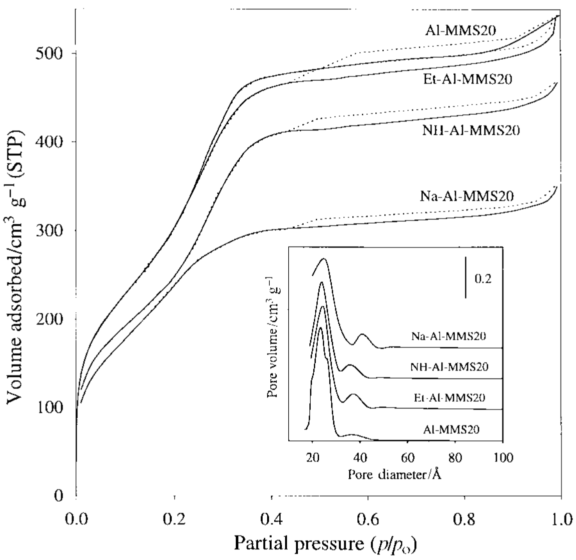

Fig. 7 Nitrogen sorption isotherms of the directly calcined Al-MMS20 sample compared to equivalent samples subjected to template extraction prior to calcination. Inset is the pore size distribution of the samples.

Al which results in lower structural ordering and therefore less well defined framework confined mesoporosity. Furthermore the mesopore filling range generally shifts to lower partial pressures as Si/Al reduces which is an indication of decrease in pore size as shown in Table 1. There is no systematic variation of interparticle or 'textural' mesoporosity (which is indicated by the presence of high pressure hysteresis)[16] with Si/Al ratio. The surface area, pore volume and average pore diameter (APD) given in Table 1 are consistent with those previously reported for similar mesoporous materials such as MCM-41.[17,18] In general the pore volume and pore sizes decrease as the amount of aluminium incorporated increases while the surface area does not change in any systematic way except for a significant reduction for the most aluminous (Al-MMS5) sample. The decrease in pore volume and pore size is probably due to some collapse of the structure (during calcination to remove the template) caused by local heating effects associated with the presence of increasing amounts of framework aluminium.[12,15] The wall thickness values obtained by subtracting the average pore diameter (APD) from the lattice parameter (a_0), are consistent with those previously reported for similar materials.[16] The wall thickness increases slightly with increasing amounts of incorporated Al which is consistent with the presence of increasing amounts of Al in the framework; the Al–O bond being longer than the Si–O bond.

Fig. 7 compares the sorption isotherms of directly calcined Al-MMS20 with equivalent materials subjected to template extraction prior to calcination. The isotherms of Et-Al-MMS20 and NH-Al-MMS20 are similar to that of the parent material indicating that these three samples have a similar extent of mesopore uniformity. The height and steepness of the mesopore filling step for Na-Al-MMS20 is lower indicating a less well defined mesopore structure. The inferior mesopore structure of Na-Al-MMS20 compared to the other samples is confirmed by the pore size distribution curves shown in Fig. 7 (inset). Furthermore as shown in Table 1, Et- and NH-Al-MMS20 samples have surface area and pore volume comparable or higher than those of the parent (directly calcined) Al-MMS20 while Na-Al-MMS20 on the other hand exhibits lower values. In addition the wall thickness of Na-Al-MMS20 at 9.7 Å, is much lower than those of the other three samples which have walls of thickness in the range 15.2 to 16.1 Å; the thinner wall for the Na-AlMMS sample is consistent with structural collapse during calcination. The textural data of the Na-Al-MMS sample is indicative of a material with lower structural ordering which is in agreement with the XRD and TGA results described earlier. The picture that emerges is that template free Na-AlMMS materials are unstable to calcination during which they undergo extensive dehydroxylation and significant structural collapse.

Nature of Al nuclei (solid state ^{27}Al NMR)

The ^{27}Al NMR spectra of the parent as-synthesised and directly calcined samples is shown in Fig. 8. The as-synthesised samples show a relatively sharp resonance at 53 ppm due to tetrahedrally coordinated Al. As expected this resonance increases with increasing incorporation of Al into the inorganic framework. Most if not all the Al is in tetrahedral coordination for samples prepared at Si/Al$\geqslant$10. The sample prepared at Si/Al ratio of 5 (Al-MMS5) exhibits a broad low intensity peak at *ca.* 0 ppm indicating that some of the Al is in octahedral coordination, *i.e.*, extra-framework Al (EFAL). Calcination in air results in some dealumination in all the samples and the amount of EFAL generally increases with lowering Si/Al ratio. In Fig. 9 we compare the ^{27}Al NMR spectra of calcined template extracted samples (prepared at Si/Al = 10) with the directly calcined sample (Al-MMS10). The spectra of the dry extracted samples (not shown) were similar to that of as-synthesised Al-MMS10 shown in Fig. 8 implying that extraction on its own had no effect on the environment of Al nuclei. The spectra of the calcined Et- and NH-Al-MMS10 samples indicate the presence of EFAL while that of Na-Al-MMS10 exhibits only one resonance at 53 ppm due to framework Al. We may therefore infer that on calcination Et- and NH-Al-MMS samples undergo some dealumination while Na-Al-MMS samples apparently retain all the Al in tetrahedral coordination. In this respect the Et- and NH-Al-MMS samples are similar to the directly calcined sample. The factor that distinguishes these three samples from Na-Al-MMS samples is that during calcination they undergo diamination. In the directly calcined and Et-Al-MMS samples the decomposing species is protonated amine while for the NH-Al-MMS sample the diaminating species are ammonium (NH_4^+) ions. Since diamination is an exothermic process it is likely that it causes local heating in the vicinity of the (framework) Al sites on which the diaminating species are attached resulting in the extraction of some of the Al. No such local

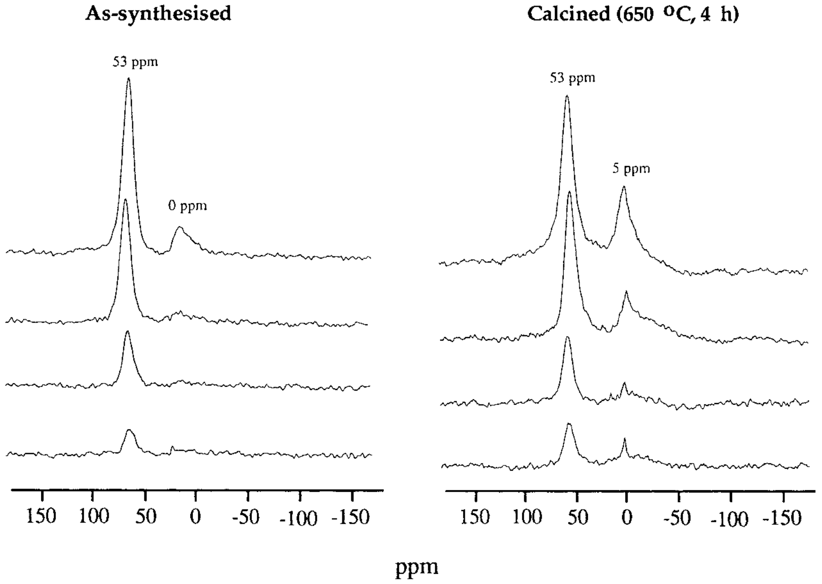

Fig. 8 ^{27}Al MAS NMR spectra of as-synthesised and calcined Al-MMS samples prepared at Si/Al ratio of (from top to bottom) 5, 10, 20, 40.

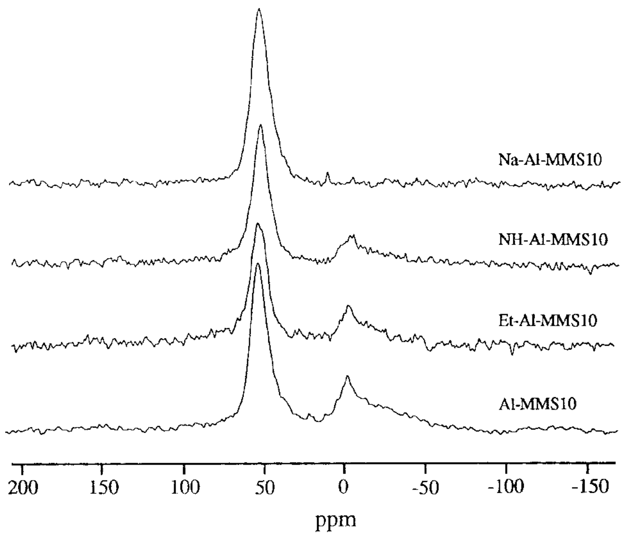

Fig. 9 ^{27}Al MAS NMR spectra of a directly calcined Al-MMS10 sample compared to equivalent samples subjected to template extraction prior to calcination.

heating effects exist for the Na-sample and therefore no dealumination occurs. Furthermore it seems that amine decomposition causes greater dealumination than the ammonium ion; from the deconvoluted NMR spectra we estimate that *ca.* 68% of the Al in the directly calcined and Et-Al-MMS10 samples is in four coordination while for the NH-Al-MMS10 sample the value is close to 78% (see Fig. 9). Presumably the diamination of the larger amine molecules causes more local heating than the decomposition of the smaller ammonium ion. Our interpretation of the NMR results suggests therefore that despite lower structural stability towards calcination, dry template free Na-Al-MMS materials are able to retain most if not all Al in tetrahedral coordination. This in turn implies that structural disintegration of Al-MMS materials is not always linked to dealumination and for calcined Na-Al-MMS materials the tetrahedral Al may exist in a disordered (or amorphous) phase as in the case of amorphous aluminosilicates. Indeed it has previously been reported that the formation of amorphous (or even crystalline alkali metal–silicate phases) can be favoured over the formation of the sodium form of AlMCM-41 if alkali cations are present during the calcination of dry relatively template free samples.[7]

Acidity and catalytic activity

The acid content of the samples was obtained using TPD of cyclohexylamine.[14,15] The results are given in Table 2. As expected the acid contents of the directly calcined materials is dependent on the Si/Al ratio and increases with the Al content. The acid contents of Et- and NH-Al-MMS samples prepared at Si/Al = 10 or 20 are similar to those of the equivalent directly calcined samples. This is in agreement with the elemental composition (see Table 1) and ^{27}Al NMR results. We may therefore assume that for Et- and NH-Al-MMS materials, template extraction prior to calcination does not have any significant effect on the population of acid sites (mainly of the Brønsted type)[14] which are strong enough to retain adsorbed cyclohexylamine after thermal treatment at 250 °C. Na-Al-MMS samples on the other hand exhibited very low acid content. This is due to the blocking of potential Brønsted acid sites by Na^+ ions which for these samples are the charge balancing cations. Na-Al-MMS samples therefore require an extra ion exchange (with ammonium ions) and calcination step to generate Brønsted acid sites.

The conversion of cumene over directly calcined Al-MMS samples as a function of time is shown in Fig. 10. The curves of some reference materials are included for comparison. The conversion achieved over the Al-MMS samples is dependent on the Si/Al ratio while the rate of deactivation is comparable for all the samples. From Fig. 10 we may conclude that the activity of hexadecylamine templated Al-MMS materials is higher than that of aluminosilicate MCM-41 and amorphous aluminosilicates but lower than that of ultra-stable Y (USY) zeolite. The activity per acid site for Al-MMS samples is given in Table 2 as the turnover frequency (TOF). The TOF values were obtained by dividing the rate of cumene conversion (μmol g^{-1} h^{-1}) after 10 minutes time on stream with the acid content (μmol g^{-1}). The TOF increases as the Al content reduces implying that the catalytic efficiency of the acid sites on Al-MMS materials reduces as their density increases. Similar trends have been observed for zeolites.[19] Fig. 11 compares the activity of the directly calcined (Al-MMS20) sample with equivalent calcined extracted samples. The Na-Al-MMS samples had no observable catalytic activity under the reaction conditions used. The initial conversion achieved by the Et-

Table 2 Acidity and catalytic activity of the study materials

		Cumene conversion	
Sample	Acidity/μmol H^+ g^{-1}	Initial rate[a]	TOF[b]
Directly calcined			
Al-MMS5	650	1830	2.82
Al-MMS10	535	1780	3.31
Al-MMS20	330	1493	4.52
Al-MMS40	210	1210	5.76
Extracted prior to calcination			
Et-Al-MMS10	520	1936	3.72
Et-Al-MMS20	320	1760	5.50
NH-Al-MMS10	550	2002	3.64
NH-Al-MMS20	330	1905	5.77
Na-Al-MMS10	80	No catalytic activity	
Na-Al-MMS20	50	No catalytic activity	

[a]Obtained after 10 min time on stream in μmol (g cat h)$^{-1}$. [b]Obtained by dividing initial rate by acid content.

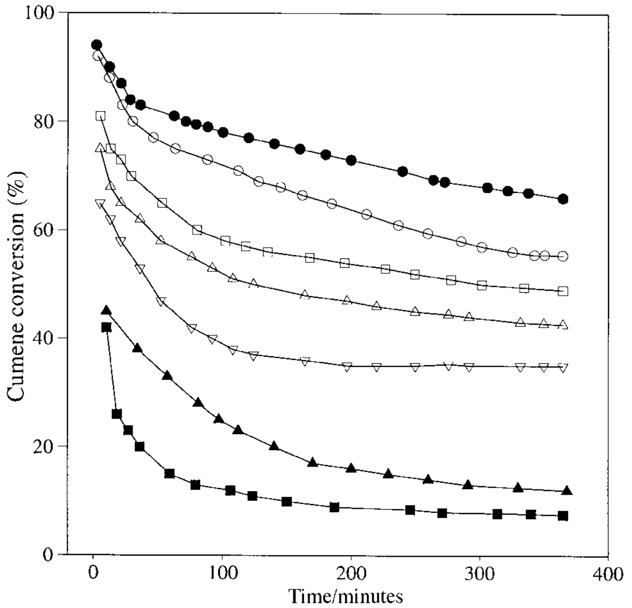

Fig. 10 Catalytic activity and deactivation behaviour of Al-MMS samples and reference materials compared at 300 °C and WHSV of 4.0. Al-MMS5 (○), Al-MMS10 (□), Al-MMS20 (△), Al-MMS40 (▽), USY (CBV740) Si/Al = 21 (●), H^+-MCM-41-20, Si/Al = 20 (▲) and amorphous silica–alumina (ASA12) Si/Al = 12 (■).

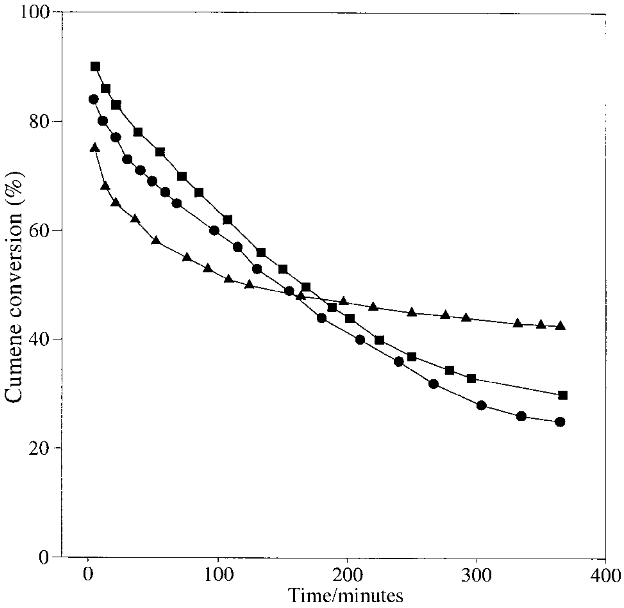

Fig. 11 Effect of template extraction on the catalytic activity and deactivation behaviour of Al-MMS samples prepared at Si/Al = 20 compared at 300 °C and WHSV of 4.0; Al-MMS20 (▲); Et-Al-MMS20 (■) and NH-Al-MMS20 (●).

and NH-Al-MMS extracted samples is higher than that of their directly calcined analogue; the order of initial conversion is Et-Al-MMS20 > NH-Al-MMS20 > Al-MMS20. This order of activity is reflected by the TOF values for the samples given in Table 2. Fig. 11 also shows that the rate of deactivation is higher for the extracted samples; this may be an indication that extracted samples possess stronger acid sites (which therefore deactivate more rapidly) than those on the directly calcined sample. The lack of catalytic activity for the Na-Al-MMS20 sample is due to the absence of Brønsted acid sites which as mentioned earlier are blocked by the charge balancing Na^+ ions.

Conclusions

Aluminosilicate mesoporous molecular sieves (Al-MMS) exhibiting short range hexagonal order have been prepared at room temperature using the primary amine hexadecylamine as structure director. The templating amine is occluded in the materials either in neutral or charged (protonated) form. The relative amounts of neutral and protonated amine depend on the Si/Al ratio. The proportion of protonated amine increases with increasing framework Al content. Template removal may be achieved by direct calcination, extraction in ethanol followed by calcination or extraction in a cation-containing ethanol solution. Extraction in ethanol alone removes only that part of the template which is not associated with framework Al while extraction in the presence of a cation results in complete template removal. Template extraction has no effect on elemental composition and for dry (non-calcined) samples results in an improvement in structural ordering. The effect of calcination depends on the mode of extraction. Samples subjected to template extraction in ethanol or ethanol/NH_4^+ are structurally stable to calcination and possess textural parameters (surface area and pore volume) similar or higher than for directly calcined samples. Samples subjected to template extraction in ethanol/Na^+ are, on the other hand, relatively unstable to calcination and undergo considerable structural degradation resulting in lower surface area and pore volume. Dealumination results from calcination of samples containing amine or ammonium ions (*i.e.*, directly calcined, ethanol and ethanol/NH_4^+ extracted samples) while Na containing (*i.e.*, ethanol/Na^+ extracted) samples do not appear to undergo any dealumination. We conclude therefore that removal of aluminium from framework positions is due to local heating effects arising from diamination of protonated amine or ammonium ions. The acid content of calcined ethanol and ethanol/NH_4^+ extracted samples is comparable to that of directly calcined samples but the former exhibit higher catalytic activity for the cracking of cumene. Calcined ethanol/Na^+ extracted samples possess very low acidity and exhibit no catalytic activity.

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References

1 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
3 Q. S. Hue, D. I. Margolese, U. Ciesla, P. Y. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
4 J. S. Beck and J. C. Vartuli, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 76.
5 C.-Y. Chen, H.-X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 17.
6 R. Schmidt, D. Akporiaye, M. Stocker and O. H. Ellestad, *Stud. Surf. Sci. Catal.*, 1994, **84**, 677.
7 S. Hitz and R. Prins, *J. Catal.*, 1997, **168**, 194.
8 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
9 R. Mokaya and W. Jones, *Chem. Commun.*, 1996, 981.
10 R. Mokaya and W. Jones, *Chem. Commun.*, 1996, 983.
11 R. Mokaya and W. Jones, *J. Catal.*, 1997, **172**, 211.
12 A. Tuel and R. Gontier, *Chem. Mater.*, 1996, **8**, 114.
13 R. J. Ray, B. L. Meyes and C. L. Marshall, *Zeolites*, 1987, **7**, 307.
14 C. Breen, *Clay Miner.*, 1991, **26**, 487.
15 R. Mokaya, W. Jones, Z. Luan, M. D. Alba and J. Klinowski, *Catal. Lett.*, 1996, **37**, 113.
16 P. T. Tanev and T. J. Pinnavaia, *Chem. Mater.*, 1996, **8**, 2068.
17 P. J. Branton, P. G. Hall, K. S. W. Sing, H. Reichert, F. Scuth and K. K. Unger, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2965.
18 J. Rathousky. A. Zukal, O. Franke and G. J. Shulzekloff, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2821.
19 M. J. Remy, D. Stanica, G. Poncelet, E. J. P. Feijen, P. J. Grobet, J. A. Martens and P. A. Jacobs, *J. Phys. Chem.*, 1996, **100**, 12440.

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