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Efficient post-synthesis alumination of MCM-41 using aluminium chlorohydrate containing Al polycations

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Aluminium chlorohydrate (ACH) which contains Al polycations such as the $Al_{13}{}^{7+}$ Keggin ion is an efficient source of Al for post-synthesis alumination of purely siliceous MCM-41 resulting in materials (herein designated AlMCM) with excellent structural integrity and enhanced acidity and catalytic activity. The amount of Al incorporated into the MCM-41 framework is dependent on the concentration of Al in the grafting solution; ^{27}Al MAS NMR confirms that a large proportion of the Al is inserted into tetrahedral positions within the framework. TEM and XPS indicate that there are no separate surface alumina phases. Alumination results in modest increases in the d_{100} basal spacing. This is accompanied by much larger reductions in pore size with the result that the pore wall thickness increases with Al content. However the alumination has little or no effect on the long range structural ordering or pore size uniformity. Alumination generates Brønsted acid sites which increase in population as the Al content rises. The ACH-grafted AlMCM materials exhibit considerable catalytic activity for cumene cracking and are superior to $AlCl_3$-grafted MCM-41 or ACH-grafted amorphous silica.

Introduction

The development of siliceous mesoporous molecular sieves such as MCM-41 has generated a lot of interest due to their potential as solid acid catalysts.[1,2] Of particular interest is their use as solid Brønsted acid catalysts; Brønsted acid sites may be generated in MCM-41 by isomorphous substitution of Al for Si during hydrothermal mixed-gel synthesis.[2,3] However, such direct mixed-gel synthesised AlMCM-41 suffer from undesirable deterioration in structural integrity.[3] Furthermore, the concentration and strength of Brønsted acid sites generated in such aluminosilicate MCM-41 materials is very low even at relatively high Al contents.[4] Much current research, therefore, focuses on post-synthesis modifications of purely siliceous MCM-41 to generate well ordered materials with acid sites on the inner walls of the mesoporous framework. We have recently reported a synthetic approach which consists of reacting the silanol groups present in the inner walls of MCM-41 with discrete amounts of aluminium alkoxide in a non-aqueous environment followed by calcination to anchor the Al.[5] Ryoo *et al.* have also reported the grafting of Al onto purely siliceous MCM-41 using non-aqueous solutions of metal salts.[6] Non-aqueous media was used due to the instability of MCM-41 in aqueous solutions. Indeed, to date the grafting of guest species onto MCM-41 has mainly been performed either in non-aqueous media or *via* vapour deposition in order to avoid the undesirable effect of water.[5–8] It is however, widely accepted that guest species are grafted onto MCM-41 *via* silanol groups;[7] therefore grafting in aqueous media is desirable because the host MCM-41 is fully hydrated thereby presenting the maximum number of silanol groups as potential grafting sites.

As part of our programme to design and synthesise MCM-41 solid acid catalysts of good structural integrity and well developed acidity we herein report the successful and efficient preparation of AlMCM-41 by reacting purely siliceous MCM-41 with aluminium chlorohydrate (ACH) solution in which the main species are Al polycations such as the $Al_{13}{}^{7+}$ Keggin ion. We report on the structural ordering, porosity, chemical composition, acidity and catalytic activity of the resulting aluminosilicate MCM-41 materials. ACH was chosen as a grafting reagent due to its well known chemistry,[9] and the fact that it forms aqueous solutions of low (acidic) pH;[10] purely siliceous MCM-41 is known to be stable in such solutions.[11] Furthermore the use of ACH ensures that only Al metal ions are present in the grafting gel and therefore precludes the presence of competing metal ions (such as Na) which may hinder the direct creation of proton/Brønsted acid sites. For this reason it is also necessary that the parent MCM-41 be free of any metal ions. In the present case MCM-41 devoid of any metal ions was obtained by using an alkali metal free MCM-41 synthetic route.

Experimental

Synthesis of materials

The parent purely siliceous MCM-41 material (designated PSMCM) was prepared as follows: tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water by stirring at 35 °C. The silica source, fumed silica (Sigma), was added to the solution under stirring for 1 h. After further stirring for 1 h the resulting synthetic gel of composition $SiO_2 : 0.25\ CTAB : 0.2\ TMAOH : 40\ H_2O$ was left to age for 20 h at room temperature following which the gel was transferred to a Teflon-lined autoclave and heated at 150 °C for 48 h. The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and calcined in air at 550 °C for 8 h to yield the parent MCM-41. For alumination 1.0 g of calcined PSMCM was added to a 50 ml solution of ACH at 80 °C and stirred for 2 h (at 80 °C). For the materials reported here, the concentration of the ACH solution (w.r.t. Al) was varied within the range 0.034–0.48 mol l^{-1}. The pH of the grafting mixtures was in the range 3.3–3.5 which favours the presence of highly polymerised Al polycations such as the $Al_{13}{}^{7+}$ Keggin ion.[9,10] The precursor Al-grafted MCM-41 was obtained by filtration and thoroughly washed with distilled water (until free of Cl^- ions), dried at room temperature and calcined in air at 550 °C for 4 h. Thorough washing of the samples, until free of Cl^- ions, is critical and in the present case it was necessary to wash with at least 5000 ml distilled water per gram of sample. Samples were prepared from ACH with Al concentrations of 0.034, 0.12, 0.24, 0.30 and 0.48 mol l^{-1} (designated AlMCM1, AlMCM2, AlMCM3, AlMCM4 and AlMCM5 respectively). For comparison

Table 1 Concentration of grafting solutions and elemental composition of the study materials. Values in parentheses are for samples obtained *via* reaction with ACH for 16 h

Sample	[Al] in grafting solution/mol l^{-1}	Si/Al
AlMCM1	0.034	17.0
AlMCM2	0.12	9.8 (6.9)
AlMCM3	0.24	7.4
AlMCM4	0.30	6.5
AlMCM5	0.48	6.1 (4.3)
AlSA[a]	0.24	9.9
PSMCM + $AlCl_3$[b]	0.24	39.0
PSMCM + $NaAlO_2$[b]	0.24	4.0

[a]Prepared by reacting (at 80 °C) amorphous silica with ACH solution containing 0.24 mol l^{-1} Al. [b]Prepared by reacting PSMCM with 0.24 mol l^{-1} solution of aluminium chloride or sodium aluminate at 80 °C.

purposes we prepared Al-grafted amorphous silica (designated AlSA) using an ACH solution of Al concentration 0.24 mol l^{-1} and also subjected PSMCM to alumination by 0.24 mol l^{-1} solutions of aluminium chloride or sodium aluminate—see Table 1 for sample details.

Characterisation

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. Elemental composition was determined using X-ray fluorescence. Textural parameters (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 analysis the calcined samples were oven dried at 120 °C and evacuated overnight at 180 °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 8–10 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.[12]

TEM images were recorded using a Jeol JEM-200CX electron microscope operating at 200 kV with a modified specimen stage with objective lens parameters $C_s = 0.41$ mm and $C_c = 0.95$ mm, giving an interpretable point resolution of *ca.* 0.185 nm. Samples for analysis were prepared by crushing the particles between two glass slides and spreading them on a holey carbon film supported on a Cu grid. The samples were briefly heated under a tungsten filament light bulb in air before transfer into the specimen chamber. The images were recorded at magnifications of 24000–49000 ×. XPS data were recorded on a VG Scientific photoelectron spectrometer using Al-K$\alpha_{1,2}$ radiation (1486.8 eV) from an X-ray source operating at 13 kV and 10 mA. Working pressure was kept below 2×10^{-8} Torr. The spectra were recorded at a photoelectron take-off angle of 45°. Binding energies were referenced to the C 1s peak from adventitious carbon surface deposits at 284.8 eV. Data processing details were as given in ref. 13.

Acidity measurements

The acid content of the materials was measured using TPD of cyclohexylamine.[14,15] 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 h 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 h. The samples were 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 280 and 450 °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.[14,15]

Catalytic testing

The cracking of cumene was performed at 300 °C and a WHSV of 5.5 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 percentage overall cumene conversion.

Results and discussion

Chemical composition

The concentration of the grafting ACH solutions (w.r.t. Al) and the elemental composition (Si/Al ratio) of the resulting aluminosilicate (AlMCM) samples are given in Table 1. Fig. 1 shows how the amount of aluminium incorporated (x_{Al}) varies with the Al available in the grafting ACH solution. Both Table 1 and Fig. 1 indicate that x_{Al} is largely dependent on the concentration of Al in the grafting solution; higher concentrations of Al in the grafting solution result in greater Al incorporation. However, x_{Al} appears to level off at high ACH concentrations suggesting the existence of a limiting factor. If we assume that Al is initially attached to the framework *via* silanol groups in the parent MCM-41,[7] it is then likely that the maximum amount of aluminium incorporated (for any given grafting conditions) is limited by the number of available and accessible silanol groups. The concept of a limiting x_{Al} value is supported by our observation that when we used much higher concentrations of Al in the grafting solution, *i.e.*, 0.84 and 1.68 mol l^{-1}, we obtained AlMCM materials with

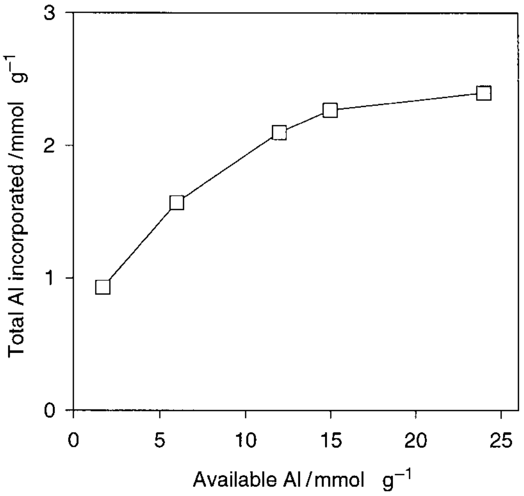

Fig. 1 Variation in the amount of aluminium incorporated into MCM-41 as a function of Al available in the grafting ACH solution.

Si/Al ratios of 4.6 and 4.2 respectively. Increasing the concentration of Al in the grafting solution above 2.0 mol l^{-1} did not result in any significant increase in x_{Al}. Indeed the lowest Si/Al ratio obtained using the present method was *ca.* 4.0. The value of x_{Al} may however, be increased by increasing the grafting time, see Table 1. We note that in both cases (using ACH solutions of 0.12 or 0.48 mol l^{-1} Al) an increase in grafting time from 2 to 16 h resulted in a similar increase in x_{Al} of *ca.* 30%. A likely explanation for this increase in x_{Al} is the presence of a greater number of silanol sites due to more extensive rehydration of PSMCM as a consequence of longer contact with the aqueous ACH solution. Indeed TGA analysis[16] of PSMCM after rehydration by stirring in water at 80 °C for 2 or 16 hours confirmed that the latter has more silanol groups. It is also possible that longer contact with the ACH solution favours greater polymerisation of Al polycations within the pores of the host MCM-41. Increasing the grafting time to 60 h, at 0.48 mol l^{-1} Al, yields AlMCM materials with Si/Al as low as 3.

Amorphous silica is much less efficient in taking up Al as evidenced by the lower Al content (Si/Al = 9.9) for a silica gel reacted with ACH containing 0.24 mol l^{-1} Al (see Table 1); similarly treated PSMCM yields AlMCM3 with a Si/Al ratio of 7.4 which is *ca.* 30% more aluminium incorporated. When AlCl$_3$ is used as the Al source, x_{Al} is much lower (Si/Al = 39) than that achieved *via* ACH (Si/Al = 7.4), see Table 1. This is in agreement with Ryoo *et al.* who, using non-aqueous solutions of AlCl$_3$, observed that the presence of water inhibited Al implantation onto MCM-41.[6] Sodium aluminate on the other hand is an excellent Al source and leads to high x_{Al}.[17] However as discussed later Na ions are also incorporated and therefore no proton (Brønsted acid) sites are generated. Our results therefore suggest that polymerised Al species (such as the $\mathrm{Al_{13}}^{7+}$ Keggin ion present in the ACH grafting solutions) are more efficient in inserting Al onto MCM-41. We however note that Al insertion using such polymerised species is best achieved at high temperature where the mobility of the bulky grafting species is enhanced; for example room temperature grafting of PSMCM using a 0.12 mol l^{-1} Al ACH solution rich in Al polycations (prepared by prior heating at 80 °C followed by cooling)[9] resulted in an AlMCM material with a Si/Al ratio of 40 compared to a Si/Al ratio of 9.8 when grafting is performed at 80 °C.

Physical characterisation

Fig. 2 shows the powder X-ray diffraction patterns of PSMCM and AlMCM samples prepared at Al concentrations of 0.12 mol l^{-1} (AlMCM2), 0.30 mol l^{-1} (AlMCM4) and 0.48 mol l^{-1} (AlMCM5). The patterns of the AlMCM samples are (in terms of peak intensity and resolution) comparable to that of the parent MCM-41 which is an indication that structural integrity is retained after Al insertion. However there is a gradual but small reduction in the intensity of the higher order peaks as Si/Al reduces. Fig. 2 also indicates that incorporation of Al results in a shift of the 100 peak to lower 2θ values and thus a higher d_{100} spacing for the AlMCM samples. This is consistent with the presence of tetrahedral Al in the MCM-41 framework and is due to the longer Al–O bond length compared to the Si–O bond. Indeed the increase in d_{100} spacing is greater at higher Al content with the consequence that the spacing increases with increasing x_{Al}, see Table 2. It is noteworthy that AlMCM materials with Si/Al ratio as low as 6.1 are obtained without any significant loss in structural integrity. Indeed TEM (see Fig. 3) confirms that structural ordering is maintained in the AlMCM materials. Fig. 3 shows the micrograph of AlMCM5 which, due to its high Al content, is expected to suffer significant structural degradation. It is clear that despite incorporating large amounts of Al, this sample (with Si/Al ratio of 6.1) still retains long range structural ordering. In direct mixed-gel synthesised AlMCM-41 such low Si/Al ratios, when obtainable, lead to a considerable decrease in ordering.[2,3]

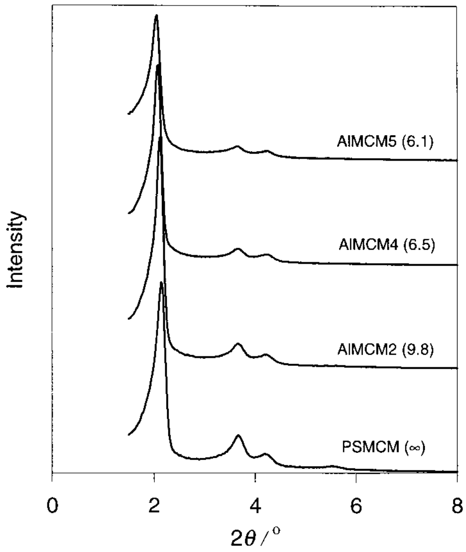

Fig. 2 Powder XRD patterns of calcined purely siliceous (PSMCM) and Al-grafted AlMCM samples. Figures in parentheses are the Si/Al ratio.

Fig. 3 HRTEM image of the Al-grafted AlMCM5 sample with a Si/Al ratio of 6.1.

The textural parameters of the parent MCM-41 (PSMCM) and the AlMCM materials are given in Table 2 while Fig. 4 shows the corresponding nitrogen sorption isotherms and pore size distribution curves for PSMCM, AlMCM2 (Si/Al = 9.8) and AlMCM5 (Si/Al = 6.1). All the samples exhibit isotherms which are typical of well ordered MCM-41.[18,19] All the isotherms show a well developed mesopore filling step in the relative pressure (p/p_0) range 0.25–0.45 which is characteristic of such structurally well ordered mesoporous materials.[18,19]

Table 2 *d*-Spacing and textural properties of purely siliceous (PSMCM) and AlMCM materials

Sample	d_{100}/Å	Surface area/ $m^2\,g^{-1}$	Pore volume/ $cm^3\,g^{-1}$	APD[a]/Å	a_o[b]/Å	Wall thickness/Å
PSMCM	41.2	887	0.85	31.6	47.6	16.0
AlMCM1	41.6	793	0.73	30.4	48.0	17.6
AlMCM2	42.0	760	0.69	29.3	48.5	19.2
AlMCM3	42.5	771	0.70	28.0	49.1	21.1
AlMCM4	42.8	767	0.65	26.5	49.4	22.9
AlMCM5	43.0	753	0.62	25.8	49.7	23.9

[a] APD = Average pore diameter (determined using BJH analysis). [b] a_o = The lattice parameter, from the XRD data using the formula $a_o = 2d_{100}/\sqrt{3}$.

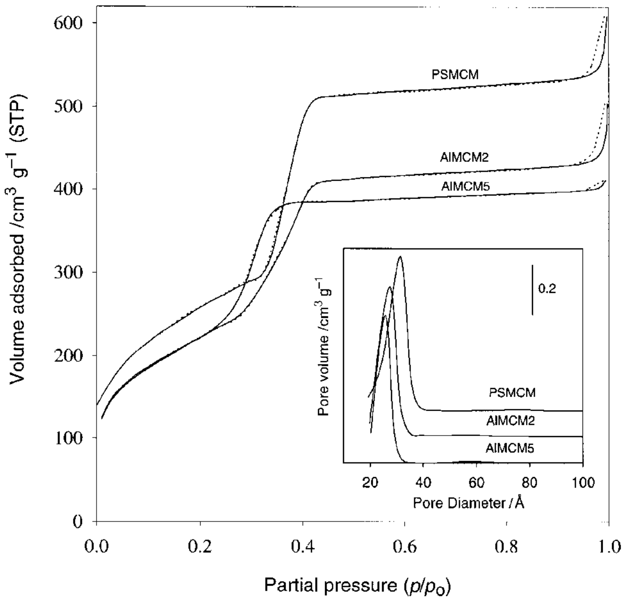

Fig. 4 Nitrogen sorption isotherms of the purely siliceous (PSMCM) and Al-grafted AlMCM samples. Inset is the corresponding pore size distribution.

The information derived from the isotherms is therefore in agreement with the XRD patterns (see Fig. 2) and points to excellent retention in structural ordering after Al insertion. The mesopore filling range generally shifts to lower partial pressures as Si/Al reduces which is an indication of a decrease in pore size as shown in Table 2 and Fig. 4 (inset). The uniformity/narrow distribution of the pores remains largely unaffected by the decrease in pore size. The textural parameters given in Table 2 are consistent with those previously reported for similar materials.[18,19] In general the surface area, pore volume and pore sizes decrease as x_{Al} increases. At 16 Å the pore wall thickness of PSMCM is comparable to the largest reported values for MCM-41.[20] On Al incorporation the wall thickness progressively increases up to 23.9 Å (for AlMCM5) which is larger than for any previously reported aluminosilicate MCM-41 material. The increase in wall thickness is at the expense of pore diameter which reduces from 31.6 Å for PSMCM to 25.8 Å for AlMCM5. Taken together the decrease in pore size and increase in wall thickness indicate that the Al is incorporated onto sites on the inner pore walls. Such Al sites are expected to generate acid sites which are easily accessible and therefore useful for catalysis. We note that part of the observed decrease in surface area and pore volume is due to increased weight of the samples occasioned by Al incorporation.[6] However despite this decrease, the lowest surface area ($753\,m^2\,g^{-1}$) and pore volume ($0.62\,cm^3\,g^{-1}$) obtained for the most aluminous sample reported (AlMCM5) are still within the range normally obtained for MCM-41 materials.

Nature of Al nuclei

^{27}Al MAS NMR of the dry and calcined AlMCM materials was performed so as to ascertain the nature and environment of the incorporated Al. The spectra given in Fig. 5 indicate that the materials contain both tetrahedrally coordinated and octahedrally coordinated Al with resonances at δ 55 and 0 respectively. For dry samples the ratio of tetrahedral Al to octahedral Al (Al_{T_d}/Al_{O_h}) is largely unaffected by the Si/Al ratio. On calcination the Al_{T_d}/Al_{O_h} ratio of the more aluminous AlMCM4 and AlMCM5 samples remains more or less the same as before calcination while for the less aluminous AlMCM2 sample the ratio increases. This increase in Al_{T_d}/Al_{O_h} suggests that for AlMCM2, dehydroxylation of hydroxy groups (such as silanols) which was induced by calcination resulted in the incorporation, into the framework, of Al in the vicinity of the silanol groups. This may be linked to the presence of a significant population of 'unused' silanols in dry AlMCM2 due to its relatively low Al content. It follows therefore that, for dry AlMCM4 and AlMCM5, there are fewer 'unused' silanols or that the distribution of the existing silanols is such that they are too far apart to act collectively in the 'capture' of Al into the framework. Nevertheless it is clear from Fig. 5 that the bulk of tetrahedrally coordinated Al is inserted into the MCM-41 framework before calcination, *i.e.*, during the 'wet' grafting in ACH. This contrasts with what we[5] and others[6] have observed when the grafting is performed in non-aqueous media, *i.e.*, that most of the Al in dry samples is octahedrally coordinated and calcination is required to anchor it into tetrahedral positions.

Owing to the relatively high content of octahedrally coordinated Al (which is usually linked to the presence of extra framework Al) we performed X-ray photoelectron spectroscopy (XPS) so as to characterise the Al species at the external surface of the AlMCM samples. XPS probes the outer layer of the particles under analysis up to a depth of *ca.* 5 nm.[21] Therefore for MCM-41 which has particle sizes ranging from 50 to 300 nm, the information provided by XPS mainly concerns the surface/near surface region. The surface Si/Al ratio and binding energies (E_b) for AlMCM5 along with data for related reference materials are given in Table 3. The surface Si/Al ratio of AlMCM5 indicates that the surface/near surface region is relatively Al-rich. The Al concentration gradient observed is compatible with the grafting procedure in which Al is 'transported' into an already formed silica framework and distributed therein. The difference between the surface and bulk Si/Al ratio is nevertheless modest and is, for example, much less than that observed for ultrastable Y (USY) zeolites such as CBV712 (see Table 3) which exhibit similar ^{27}Al MAS NMR spectra.[21]

The Si 2p, Al 2p and O 1s binding energies of AlMCM5 suggests a surface/near surface composition intermediate between zeolite-Y (CBV300) and USY (CBV 712),[21] see Table 3. This implies that the Al in the surface/near surface region of AlMCM5 is somewhat associated with the MCM-41 framework and does not necessarily form a separate phase. Indeed TEM of AlMCM5 did not reveal the presence of any

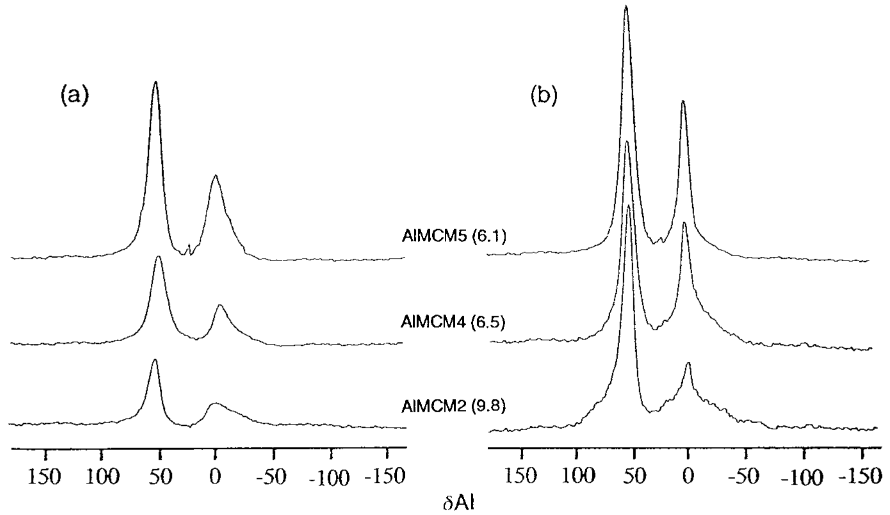

Fig. 5 ^{27}Al MAS NMR spectra of (a) dry and (b) calcined Al-grafted AlMCM samples. Values in parentheses are the Si/Al ratio.

Table 3 Surface Si/Al ratio and binding energies for AlMCM5 and related reference materials

			E_b/eV		
Sample	Si/Al$_{Bulk}$	Si/Al$_{XPS}$	Si 2p	Al 2p	O 1s
AlMCM5	6.1	4.1	102.6	74.8	532.6
USY (CBV712)[a]	5.8	2.9	103.2	75.0	532.5
Zeolite Y (CBV300)[a]	2.6	3.4	102.1	74.4	531.8

[a] Data from ref. 21.

Table 4 Acidity and catalytic activity of the study materials. Values in parentheses are for samples obtained *via* reaction with ACH for 16 hours

		Cumene conversion	
Sample	Acidity/ μmol H$^+$ g^{-1}	Initial rate[a]	TOF[b]
AlMCM1	385	390	1.01
AlMCM2	470 (560)	516 (591)	1.10 (1.05)
AlMCM3	540	754	1.40
AlMCM4	570	819	1.44
AlMCM5	605 (616)	897 (978)	1.48 (1.59)
AlSA[c]	295	184	0.62
PSMCM + AlCl$_3$[d]	212	46	0.22
PSMCM + NaAlO$_2$[d]	Trace	No catalytic activity	

[a] Obtained after 10 min time on stream in μmol (g cat h)$^{-1}$. [b] Obtained by dividing initial rate with acid content. [c] Prepared by reacting (at 80 °C) amorphous silica with ACH solution containing 0.24 mol l^{-1} Al. [d] Prepared by reacting PSMCM with 0.24 mol l^{-1} solution of aluminium chloride or sodium aluminate at 80 °C.

Al-rich dense phases similar to those observed by Kloetstra *et al.*[22] The XPS results are therefore not compatible with the presence of large amounts of (surface) octahedrally coordinated extra framework Al. Concerning the NMR results it is important to note that the calcined samples were fully hydrated and equilibrated with room air prior to analysis. The rehydration, as previously reported for zeolites[23] may convert some tetrahedral Al to octahedral Al; this conversion may account for the apparently high content of octahedrally coordinated Al inferred from the NMR spectra. We note that when AlMCM5 was subjected to refluxing in boiling water for 16 h the bulk Si/Al ratio reduced from 6.1 to 5.1 indicating that silica (and not Al) was preferentially leached out during the refluxing. Since the refluxing did not have any significant effect on the $\mathrm{Al}_{T_d}/\mathrm{Al}_{O_h}$ ratio, coupled with the fact that the structure remained intact[24] it is likely that the extracted silica was not from the framework but may have existed as an amorphous silica phase. Taken together these observations indicate that the Al incorporated into AlMCM samples is not easily removed as might be expected if a large proportion of it existed as a separate phase of extra framework Al. It is therefore likely that any 'non-framework' octahedrally coordinated Al in these samples is partially connected to the framework as has been previously observed for zeolites[23] and recently suggested for MCM-41.[25]

Acidity and catalytic activity

The acid content of AlMCM and reference materials as determined using temperature programmed desorption of cyclohexylamine is given in Table 4. The weight loss between 280 and 450 °C was used to compute the acid content given in μmole H$^+$ g^{-1} assuming that each base molecule interacts with one acid site. The incorporation of Al generates acid sites and the number of acid sites generated increases with x_{Al}. In general the acid content of the AlMCM samples is much higher than that of equivalent (in terms of Si/Al ratio) AlMCM-41 obtained from direct mixed gel synthesis[2,26] but comparable to that of AlPSMCM materials prepared *via* grafting of Al (from Al alkoxides) onto PSMCM in non-aqueous media.[5] Analysis of the increase in acid content as a function of x_{Al} reveals an approximately linear relationship which is compatible with our interpretation of the NMR and XPS data and points to a scenario where 'non-framework' Al (upto bulk Si/Al = 6.1) might be partially attached to the framework and contributes to the creation of acid sites. This contrasts with what we observed for AlPSMCM samples (prepared *via* grafting of Al from Al alkoxides onto PSMCM in non-aqueous media) for which the acid content appeared to reach a plateau at a lower Al content (*i.e.*, at a Si/Al ratio of 10).[5] We propose that in the present case the use of aqueous media ensures that the parent MCM-41 is extensively rehydrated and therefore presents more anchoring sites (*e.g.* silanols) for Al. It follows therefore that the rehydrated MCM-41 is able to 'accommodate' more Al into acid generating sites.

The acid content of Al-grafted amorphous silica (AlSA) is less than that of either AlMCM3 (which is equivalent in terms of preparation) or AlMCM2 which contains a similar amount of Al, see Table 4. Despite a high x_{Al}, the sample prepared using sodium aluminate presents practically no (Brønsted) acid content. We attribute this to the presence of Na$^+$ ions which occupy any potential Brønsted acid sites. This observation emphasises the importance of excluding alkali metal ions during the grafting process if proton sites are to be generated directly. Indeed the presence of even small amounts

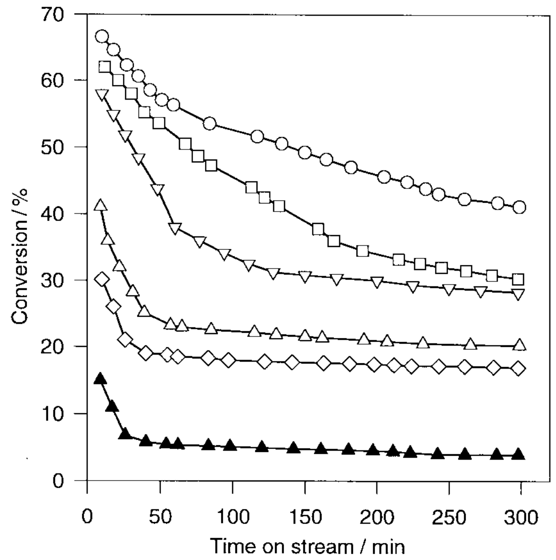

Fig. 6 Deactivation behaviour during cumene conversion over AlMCM samples and a reference material (AlSA) compared at 300 °C. AlMCM5 (○), AlMCM4 (□), AlMCM3 (▽), AlMCM2 (△), AlMCM1 (◇) and AlSA (▲).

(< 1 wt%) of Na in the parent MCM-41 inhibits the creation of proton sites; when we used purely siliceous MCM-41 (prepared using the method of Ryoo and Kim[27]) which contained residual Na we found that although Al was incorporated into the MCM-41 framework, the acid content of the resulting AlMCM samples was very low.

The superior acidity of the AlMCM samples (compared to the reference materials) was confirmed by their activity in the cracking of cumene as shown in Table 4 and Fig. 6. Under the conditions used, the reaction proceeded almost exclusively *via* catalytic cracking (on Brønsted acid sites) to benzene and propene. Only trace amounts of α-methylstyrene, which may be formed *via* dehydrogenation of cumene on Lewis acid sites, were obtained. The reaction is therefore a good probe for Brønsted acidity.[2,14,28] The catalytic activity of AlMCM materials generally increases with increase in acid content (and therefore x_{Al}). The modest increase in TOF, as Si/Al reduces, indicates that the strength of Brønsted acid sites generated on AlMCM materials is only slightly influenced by Al content. ACH (0.24 mol l^{-1} Al) grafted amorphous silica (AlSA) exhibited much lower activity compared to both AlMCM3 (which was prepared using a similar ACH solution) or AlMCM2 which contained a similar amount of aluminium. When $AlCl_3$ was used as Al source the resulting material presented poor catalytic activity and very low TOF. We note that the acid content of the $AlCl_3$-grafted MCM-41 is reasonable for its Al content; however its TOF is very low which means that the acid sites are not as effective as those on ACH-grafted materials. This implies either or both of the following: (i) poor accessibility of the acid sites and/or (ii) lower acid strength. The material grafted using sodium aluminate exhibited no catalytic activity despite a very high x_{Al} due to the absence of Brønsted acid sites. Fig. 6 shows the variation of cumene conversion as a function of time on stream and indicates that all the AlMCM samples deactivate to a significant extent. The more aluminous AlMCM5 and AlMCM4 samples continuously deactivate over 5 h. On the other hand the samples with lower amounts of aluminium incorporated (AlMCM2 and AlMCM1) undergo deactivation during the first hour only after which the conversion remains more or less constant. Sample AlMCM3 exhibits intermediate deactivation behaviour.

Conclusions

Aluminosilicate MCM-41 materials have been prepared by reacting purely siliceous MCM-41 with dilute aqueous solutions of aluminium chlorohydrate (ACH) (also known as chlorhydrol). The ACH solutions, which contain Al polycations (such as the Al_{13}^{7+} Keggin ion), are an efficient source of Al for such post-synthesis alumination of purely siliceous MCM-41. The resulting aluminosilicate materials (herein designated AlMCM) retain the structural integrity of the parent purely siliceous MCM-41 and possess enhanced acidity and catalytic activity. The amount of Al incorporated into the MCM-41 framework is dependent on the concentration of Al in the grafting solution. However, for any given set of grafting conditions the amount of Al incorporated is limited by the number of silanol groups (which act as the anchoring sites) available on the parent MCM-41. The amount of Al incorporated may, however, be increased by performing the grafting over longer periods of time. ^{27}Al MAS NMR confirms that a large proportion of the Al is inserted into tetrahedral positions within the MCM-41 framework. TEM and XPS indicate that there are no separate surface alumina phases. The incorporation of Al results in modest increases in the d_{100} basal spacing. This is accompanied by much larger decreases in pore size which means that the pore wall thickness increases with increasing Al incorporation. However, the long range structural ordering and pore size homogeneity remain largely unaffected by the decrease in pore size. The incorporation of Al generates Brønsted acid sites which increase in population as the Si/Al ratio decreases. The presence of metal ions such as Na in the grafting gel hinders the creation of Brønsted acid sites. The ACH-grafted AlMCM materials exhibit considerable catalytic activity for cumene cracking and are superior to equivalent $AlCl_3$-grafted MCM-41 or ACH-grafted amorphous silica materials.

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