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X. S. Zhao

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SURFACE ALUMINATION OF MESOPOROUS SILICATES

ROBERT MOKAYA

*School of Chemistry, University of Nottingham, University Park,
Nottingham NG7 2RD, UK*

E-mail: r.mokaya@nottingham.ac.uk

The primary aim of introducing Al onto mesoporous silicates is to create acid and ion exchange sites. The traditional method of preparing mesoporous aluminosilicates is via direct (mixed-gel) synthesis during which an aluminosilicate framework is formed directly from aluminate and silicate ions. An alternative and increasingly popular method of introducing Al onto mesoporous silicates is the so-called post-synthesis alumination, in which the Al is grafted onto an already formed silica framework. This is possible due to the presence of silanol groups on the mesoporous silica pore walls, which act as anchoring sites for the Al. Post-synthesis alumination generates aluminosilicate materials with readily accessible acid or ion exchange sites on the inner walls of the mesoporous framework and generally offers distinct advantages over direct synthesis with respect to accessibility of active sites, structural ordering and stability.

1 Introduction

Mesoporous silicas possess uniform channels of diameter in the range 20Å to 500Å and are synthesised via a mechanism in which supramolecular assemblies of surfactant micelles act as structure directors for the organisation of inorganic silicate precursors [1]. There is currently considerable research interest in the preparation and use of heteroatom containing mesoporous silicas as heterogeneous catalysts, ion exchangers, molecular/supramolecular sieves or templates for the preparation of mesostructured non-silica materials or other nanostructured arrays [1,2]. The incorporation of Al is particularly important as it gives rise to solid acid materials with acid sites associated with the presence of Al in framework positions within the silica pore walls. Mesoporous aluminosilicates have therefore been the focus of many recent studies [3-6], because of their potential application in solid acid/base catalysis and adsorption technology and in particular as acid catalysts for bulk hydrocarbon conversion. The traditional method of introducing Al into mesoporous silicates is by direct (mixed-gel) synthesis during which an aluminosilicate framework is formed directly from aluminate and silicate ions.

An alternative method of introducing Al onto mesoporous silicates is via post-synthesis alumination, in which the Al is grafted onto an already formed silica framework. Silanol groups on the pore walls of the 'host' silica framework act as anchoring sites for the Al. This review covers the developments in post-synthesis alumination of mesoporous silica since the first reports appeared about five years ago. It also contains a brief mention of directly prepared materials and draws comparisons between the two methods of preparing mesoporous aluminosilicates.

2 Direct mixed-gel synthesised mesoporous aluminosilicates

The primary aim of introducing Al onto mesoporous silicas is to create acid sites and ion exchange capacity associated with tetrahedrally coordinated Al located within the aluminosilicate framework. In the case of direct mixed-gel synthesis, once the Al is incorporated into the silica framework, the acid (Bronsted and Lewis) and ion exchange sites are generated via one of two ways; (i) cation exchange of the calcined material with ammonium ions followed by further calcination or (ii) calcination for as-synthesised materials that do not contain any alkali ions. The amount of Al incorporated (usually given by the molar Si/Al ratio) is governed by the concentration of aluminate species in the synthesis gel. Varying the Si/Al ratio can therefore control the number of acid or ion exchange sites generated. In general, the number of acid sites increases with the Al content (or more precisely the accessible tetrahedral Al content). The acid strength tends to be largely independent of the Al content. The acid strength of directly prepared aluminosilicates is generally low and comparable to that of amorphous aluminosilicas.

A number of studies and recent reviews have dealt with the preparation and characterization of direct (mixed-gel) synthesised mesoporous aluminosilicates [3-26]. In general, directly prepared mesoporous aluminosilicates exhibit the highest acidity and catalytic activity for acid catalysed reactions at high Al contents. High Al contents however have the disadvantage of compromising the structural ordering and are usually accompanied by a significant degradation of structural ordering especially after thermal treatments (e.g. calcination during template removal) [7,13-16]. The degradation in structural ordering is usually an indication of poor thermal stability of the aluminosilicate framework and in particular low stability of tetrahedrally co-ordinated (framework) Al. Aluminium in tetrahedral framework positions is crucial for the generation of acid sites. The extent of Al incorporation into framework (as opposed to non-

framework) positions can, to some extent, be controlled since it is dependent of the Al source used [17-26]. Once incorporated into framework positions it is desirable that the Al is stable (especially to thermal and hydrothermal treatments) within tetrahedral positions. The decrease in structural ordering with Al content in mesoporous aluminosilicates is usually accompanied by an increase in the amount of non-framework Al. The increase of non-framework Al is occasioned by dealumination – the extraction of Al from the framework due mainly to local heating effects. Dealumination is associated with a decrease in the ion exchange capacity and the number of Bronsted acid sites.

3 Methods for the surface alumination of mesoporous silicas

The direct mixed-gel synthesis of mesoporous aluminosilicates suffers from irreproducible preparation routes which result in materials with poor structural ordering and low thermal stability (especially with respect to the stability of Al in framework positions). Another disadvantage of direct mixed-gel synthesis of mesoporous aluminosilicates is that some of the Al is incorporated deep within the pore walls where it is not readily accessible and does not generate acid or ion exchange sites. These disadvantages can be addressed by preparing the mesoporous aluminosilicates via routes which graft Al onto an already prepared silica host matrix. Klinowski and co-workers [27] aluminated pure silica MCM-41 using an aqueous solution of sodium aluminate (NaAlO_2) and obtained materials with framework Si/Al ratio as low as 1.9. ^{27}Al and ^{29}Si magic-angle-spinning (MAS) NMR showed that all the aluminium was incorporated in the framework. Their aluminated materials retained good structural ordering as indicated by well-resolved X-ray diffraction (XRD) patterns. The pore size of the aluminated MCM-41 was observed to decrease at high Al contents. Both the NaAlO_2 concentration and temperature were found to be key variables in the alumination. Treatment with a concentrated ($>1 \text{ mol l}^{-1}$) solution of NaAlO_2 at ca. 100°C transformed the pure silica MCM-41 into crystalline zeolite Na-A. It is worth noting that due to the presence of Na in the aluminating reagent, these materials required an extra ammonium ion exchange and calcination step to generate acid sites [28].

Two groups independently reported the first preparation of aluminated mesoporous silicates where acid sites were generated simply by calcination without the need for ammonium exchange [29-31]. Mokaya and Jones reported the preparation of Al-containing MCM-41 materials by grafting Al onto purely siliceous MCM-41 [29,30]. The grafting was performed

using aluminium isopropoxide as Al source and hexane as solvent. ^{27}Al MAS NMR and XPS were used to confirm that the Al was incorporated (before and especially after calcination) into the solid framework where it adopted 4-coordinate symmetry as shown in Figure 1. The resulting Al-grafted MCM-41 materials retained the structural ordering (with no loss of long range ordering) and physical properties of the parent pure silica MCM-41 [29,30]. Ryoo and co-workers [31] on the other hand, reported a post-synthesis route, through which various metal elements could be grafted onto pure silica mesoporous frameworks using non-aqueous solutions of various metal salts to obtain mesoporous metallosilicates with superior structural integrity, acidity and catalytic activity compared to equivalent materials prepared via direct mixed-gel synthesis. Calcination of AlCl_3 -grafted MCM-41 yielded mesoporous aluminosilicates with a high proportion of Al in tetrahedral positions as shown in Figure 2.

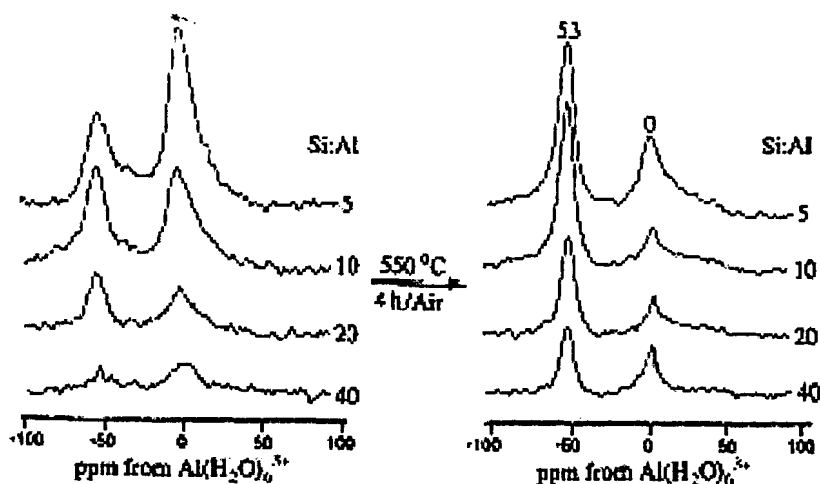


Figure 1. ^{27}Al MAS NMR spectra of dry (left) and calcined (right) Al-grafted MCM-41 materials prepared by reacting pure silica MCM-41 with aluminium isopropoxide in hexane [30].

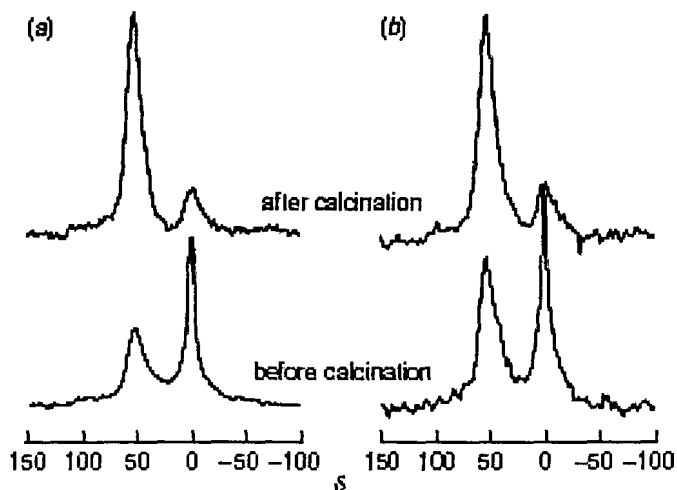


Figure 2. ^{27}Al MAS NMR spectra for Al-grafted samples: (a) Al-MCM-41 ($\text{Si}/\text{Al} = 32$) (b) AIKIT ($\text{Si}/\text{Al} = 33$). The NMR spectra show transitions from octahedral to tetrahedral Al upon calcination [31].

Mokaya and Jones extended post-synthesis aluminations of mesoporous silicas to aqueous solutions [32,33]. Aluminosilicate MCM-41 materials were prepared by reacting purely siliceous MCM-41 with dilute aqueous solutions of aluminium chlorohydrate (ACH) [32,33]. The ACH solutions, which contain Al polycations (such as the Al_{13}^{7+} Keggin ion) as the main Al species were found to be an efficient source of Al for aluminations of MCM-41. The amount of Al grafted onto the MCM-41 was largely dependent on the concentration of Al in the grafting solution as shown in Table 1. In general, higher concentrations of Al in the grafting solution result in greater Al incorporation. However, the amount of grafted Al levelled off at high ACH concentrations suggesting the existence of a limiting factor, which was thought to be the number of available and accessible silanol groups present on parent MCM-41. The resulting aluminosilicate materials had textural properties similar to those of the parent pure silica MCM-41 (PSMCM) as shown in Table 1. The aluminated samples also retained the structural integrity of the parent pure silica MCM-41 as shown in Figure 3.

Table 1. Elemental composition (Si/Al ratio) and textural properties of pure silica (PSMCM) and Al-MCM-41 materials prepared by post-synthesis alumination of PSMCM using aqueous solutions of aluminium chlorohydrate (ACH) [33].

Sample	[Al] ^a	Si/Al	d_{100} ^b (Å)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	APD ^c (Å)	a_0 ^d (Å)	WT ^e (Å)
PSMCM			41.2	887	0.85	31.6	47.6	16.0
AlMCM1	0.034	17.0	41.6	793	0.73	30.4	48.0	17.6
AlMCM2	0.12	9.8	42.0	760	0.69	29.3	48.5	19.2
AlMCM3	0.24	7.4	42.5	771	0.70	28.0	49.1	21.1
AlMCM4	0.30	6.5	42.8	767	0.65	26.5	49.4	22.9
AlMCM5	0.48	6.1	43.0	753	0.62	25.8	49.7	23.9

^aConcentration of Al (mol l⁻¹) in grafting ACH solution. ^b d_{100} = basal (100) spacing. ^cAPD = Average Pore Diameter (determined using BJH analysis).

^d a_0 = The lattice parameter from XRD data, using the formula $a_0 = 2d_{100}/\sqrt{3}$. ^eWall thickness, given by $a_0 - \text{APD}$.

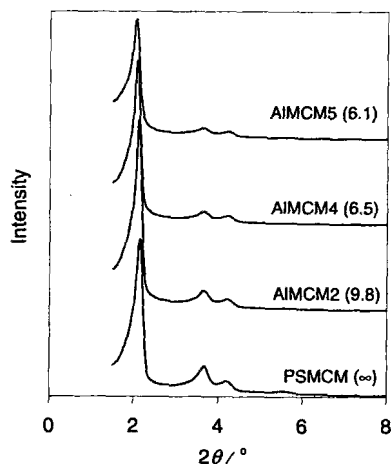


Figure 3. Powder XRD patterns of calcined pure silica MCM-41 (PSMCM) and Al-grafted MCM-41 materials prepared by reaction of PSMCM with an aqueous solution of aluminium chlorohydrate. Values in parenthesis are the Si/Al ratio of the Al-grafted samples [33].

Post-synthesis aluminations are generic and may be applied to all types of mesoporous silicas. For example, Cheng *et al* [34] aluminated pure silica SBA-15 through reaction with aluminum chloride. Al was incorporated into the framework of the SBA-15 with no deterioration in structural ordering. Luan and co-workers [35] performed post-synthesis aluminations of mesoporous silica SBA-15 via three different procedures, i.e., reaction with (i) AlCl_3 in dry ethanol [31] (ii) aluminum isopropoxide in dry hexane [29,30] and (iii) an aqueous solution of sodium aluminate [28]. They evaluated the efficiency of the aluminations and their effect on the pore structure and ion exchange capacity of the resulting Al-SBA-15. They compared the amount of framework and non-framework Al, at various Si/Al ratios for samples prepared via the three aluminations and found that, in general, aluminations by aqueous sodium aluminate was the most effective in grafting the Al into tetrahedral positions. Materials prepared using sodium aluminate however had the disadvantage of the presence of Na, which hindered the generation of acid sites via simple calcination. Aluminations by AlCl_3 in ethanol maintained the mesoporous structure of SBA-15 best. Electron-spin resonance studies revealed that the incorporated Al in the tetrahedral framework serve as ion exchange sites [35]. In a similar comparative study, Chen *et al* [36] prepared Al-MCM-41 materials via post-synthesis aluminations of pure silica MCM-41 using various Al sources, i.e., AlCl_3 , aluminum isopropoxide and NaAlO_2 . They found that irrespective of the preparation method, the surface area, pore diameter, crystallinity and thermal stability of the Al-MCM-41 materials decreased with increasing Al content. The aluminated materials had better thermal stability and could incorporate higher amounts of Al without disintegration of the mesoporous structure compared to Al-MCM-41 prepared by direct synthesis. For example, directly prepared samples did not exhibit mesoporous structural ordering at Si/Al ratios lower than 5 while for post-synthesis aluminations with AlCl_3 or Al isopropoxide it was possible to achieve Si/Al ratios lower than 5 with retention of the mesoporous structure.

Post-synthesis aluminations of pure silica MCM-41 and SBA-15 may also be performed using trimethylaluminum (TMA) as Al source and dry toluene as solvent [37,38]. Sano *et al* found that with TMA as aluminating reagent, Al was easily incorporated (without the need for calcination) into the silica framework of MCM-41 and SBA-15 without severe structural degradation. However, the basal (d_{100}) spacing, surface area and pore volume of the aluminated SBA-15 decreased monotonously with the extent of aluminations (Table 2). The incorporation of Al into tetrahedral

positions was higher for MCM-41 as shown in Figure 4, which compares the ^{27}Al MAS NMR of TMA aluminated, SBA-15 and MCM-41.

Table 2. Characteristics of pure silica SBA-15 and AlSBA-15 prepared by post-synthesis alumination with trimethylaluminium (TMA) followed by calcination at 773 K for 5 hours [37].

Sample	[TMA] ^a	Si/Al ^b	d_{100} ^c (nm)	Surface Area (m ² /g)	Pore Volume ^d (cm ³ /g)	Pore Size ^d (nm)	a_0 ^e (nm)	WT ^f (nm)
SBA-15			9.80	770	0.811	6.16	11.31	5.15
AlSBA-15	1	14.6	9.52	613	0.693	6.16	10.99	4.83
AlSBA-15	2	8.4	9.52	526	0.654	6.16	10.99	4.83
AlSBA-15	3	5.7	9.43	457	0.598	6.16	10.89	4.73
AlSBA-15	4	4.9	9.43	432	0.585	5.80	10.59	5.09
AlSBA-15	5	4.8	9.43	410	0.564	5.80	10.89	5.09

^a Amount of TMA (mmol) in alumination mixture. ^b Bulk Si/Al determined by X-ray fluorescence. ^c d_{100} = basal (100) spacing. ^d Determined by the Dollimore-Heal method. ^e a_0 = Lattice parameter from SAXS data, using the formula $a_0 = 2d_{100}/\sqrt{3}$. ^f Wall thickness = a_0 – pore size

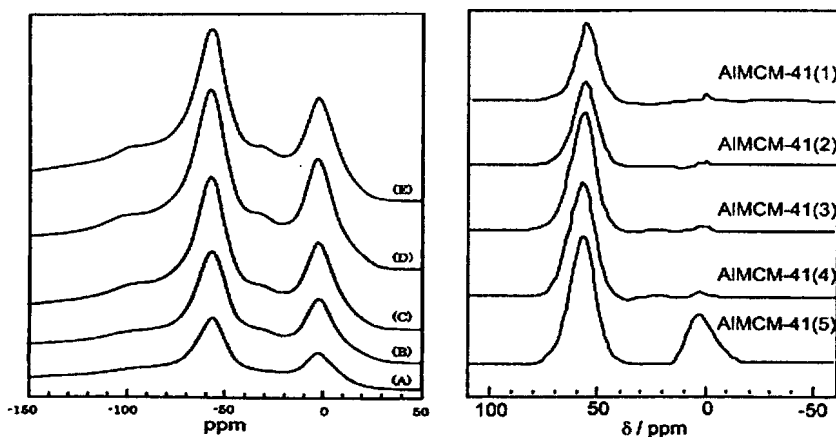


Figure 4. ^{27}Al MAS NMR spectra for TMA-grafted SBA-15 (left) and MCM-41 (right). For SBA-15; (A) 1 mmol TMA, Si/Al = 14.6, (B) 2 mmol TMA, Si/Al = 8.4, (C) 3 mmol TMA, Si/Al = 5.7, (D) 4 mmol TMA, Si/Al = 4.9, (E) 5 mmol TMA, Si/Al = 4.8 and for MCM-41; (1) 1 mmol TMA, Si/Al = 14.3, (2) 2 mmol TMA, Si/Al = 9.0, (3) 3 mmol TMA, Si/Al = 6.3, (4) 4 mmol TMA, Si/Al = 4.3 and (5) 5 mmol TMA, Si/Al = 4.0 [37,38].

Dwyer and co-workers [39] carried out a detailed study of the vapour phase alumination (using AlCl_3 vapour) of pure silica MCM-41 and compared the resulting materials with directly prepared Al-MCM-41. Al was successfully incorporated into pure silica MCM-41 via post-synthesis reaction with AlCl_3 vapour as grafting reagent. ^{27}Al and ^{29}Si MAS NMR studies indicated that presence of both framework and extra-framework Al sites in the AlCl_3 vapour aluminated samples. Ryoo and co-workers [40] prepared three different types of Al-containing materials, KIT-1, MCM-41 and MCM-48 in which the Al was incorporated by various routes such as direct syntheses, grafting of the Al species with anhydrous AlCl_3 , and impregnation with an aqueous solution of AlCl_3 . ^{27}Al MAS NMR spectroscopy indicated that, for impregnated samples, the co-ordination of Al sites lost tetrahedral symmetry upon complete dehydration, suggesting the possible existence of three-coordinated Al catalytic sites.

Mokaya investigated the effect of particle size on the post-synthesis alumination of pure silica MCM-41 [41]. Aluminosilicate MCM-41 materials derived from pure silica MCM-41 materials of varying particle size were prepared via post-synthesis grafting routes. Particle size was found to have no effect on the take-up and retention of Al (similar Si/Al molar ratios were obtained for various particle sizes) but influenced the distribution of Al with larger particles having a higher concentration of surface Al. Small particles were therefore 'penetrated' by Al to a much greater extent than large particles. Physical characterisation (XRD and N_2 sorption studies) indicated that particle size played a key role in determining whether or not structural integrity is retained after Al insertion; large particle pure silica MCM-41, with long range ordering, was more likely to retain structural ordering and retain textural properties after Al insertion. The acid content (and therefore proportion of Al sites giving rise to acid sites) was, however, higher in smaller particle samples than in large particle samples. However particle size had no effect on acid strength. The activity for acid catalysed reactions (cracking of cumene) was higher for small particle samples. This was attributed to the higher efficiency with which reactant and product molecules access or exit the shorter pores in small particles as opposed to the longer (one-dimensional for MCM-41) pores in the larger particles.

The temperature at which alumination is performed is also an important factor which influences the properties of resulting mesoporous aluminosilicates. Mokaya [42] probed the influence of temperature on the alumination process. Al-grafted MCM-41 materials were obtained by reacting pure silica MCM-41 with aqueous solutions of aluminium chlorohydrate (ACH) at either room temperature (RT) or 80°C [42]. The

grafting temperature was found to have a profound effect on physical, chemical and catalytic properties. Good retention of structural integrity was achieved after grafting at 80°C while materials prepared at RT suffered much greater structural degradation. Incorporation of Al was up to four times higher at 80°C than at RT. The large variation between the amounts of Al incorporated at 80°C and RT was ascribed to differences in the mobility of the rather bulky Al species found in ACH solutions. The higher Al content of materials grafted at 80°C translated to higher acid content and higher total conversions for the cracking of cumene. However the catalytic activity per active site (TOF values) was higher for RT grafted materials presumably due to better site isolation occasioned by a lower Al content [42].

Alumination of mesoporous silicas via post-synthesis grafting procedures in aqueous or non-aqueous media normally results in uniform incorporation of Al with little control of its spatial distribution. Increasing the Al content in the alumination gel generally results in a uniform increase in the amount of incorporated Al throughout the surface of the entire sample. Using a template-directed alumination procedure, Mokaya [43] described an unusual stepwise alumination procedure in which increasing proportions of pure silica MCM-41 are aluminated depending on the amount of Al available in the alumination gel. In the so-called template-directed alumination of MCM-41, the Al was introduced onto pure silica MCM-41 during secondary synthesis (i.e., recrystallisation). The extent of alumination, up to full alumination, increased with the amount of Al in the recrystallisation gel. Evidence from several characterisation techniques indicated that during the recrystallisation in the presence of an Al source, the proportion of aluminated MCM-41 increased with increase in the content of Al in the recrystallisation gel and that beyond a certain gel Si/Al ratio (determined by synthesis conditions) the whole sample was aluminated. The findings hinted at the possibility of full alumination a portion of the pores of pure silica MCM-41 before alumination of other pores has started resulting in an apparently mixed-phase material with clearly defined basal spacings as shown in Figure 5 [43].

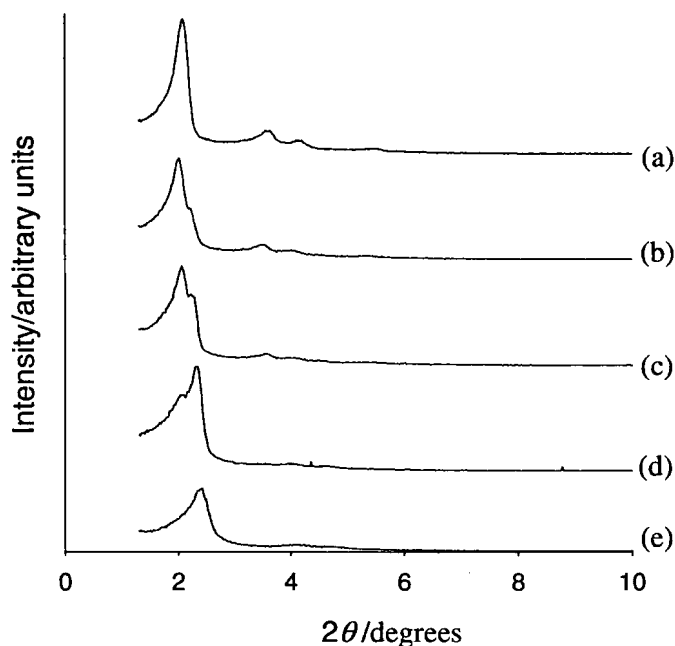


Figure 5. Powder XRD patterns of (a) pure silica Si-MCM-41 and recrystallised (b) Al-MCM41-80, Si/Al = 40.1; (c) Al-MCM41-40, Si/Al = 28.3; (d) Al-MCM41-20, Si/Al = 16.9 and (e) Al-MCM41-10, Si/Al = 8.8, materials [43].

Mesoporous aluminosilicates prepared via surface alumination tend to have significant amounts of extra-framework Al (EFAL). Reinsertion of such EFAL into the framework is desirable. Indeed the reinsertion of EFAL into framework positions is a well-known phenomenon for dealuminated Y zeolites and is achieved via, for example, hydrothermal treatment of the zeolite in an aqueous solution of KOH [44]. However, such treatment is not feasible for mesoporous aluminosilicates because it is too severe. The relatively fragile mesoporous frameworks would readily dissolve in the highly basic (pH = 13.5) KOH solution. Mokaya [45] reported on a modified 'insertion' method suitable for mesoporous aluminosilicates. The method allowed for virtually all octahedrally coordinated (extra-framework) Al in calcined Al-grafted MCM-41 materials (designated CAP5, Si/Al = 4.6 and CAH5, Si/Al = 4.7) to be inserted into (tetrahedral) framework positions as shown in Figure 6. The method involved treatment of the Al-grafted materials with an aqueous solution of NH_4OH (pH ~ 11.1) and could be performed at either room temperature

(30°C) or at a range of temperatures up to 80°C. The insertion of EFAL into the Al-grafted MCM-41 framework increased the proportion of tetrahedrally coordinated Al with a concomitant increase in acidity and ion exchange capacity [45].

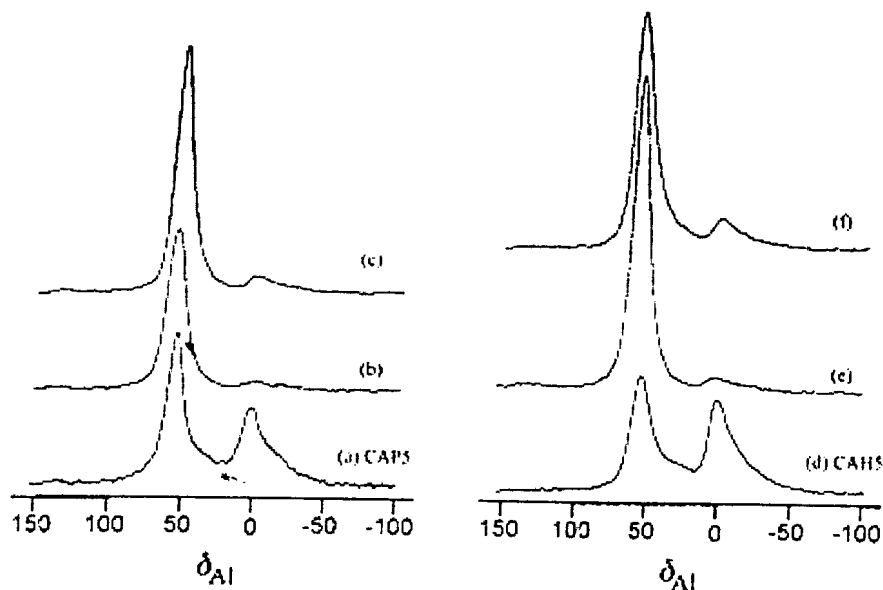


Figure 6. ^{27}Al MAS NMR spectra of Al-grafted materials before and after treatment with NH_4OH ; (a) CAP5, (b) CAP5 treated at 30°C, (c) CAP5 treated at 80°C, (d) CAH5, (e) CAH5 treated at 30°C and (f) CAH5 treated at 80°C [45].

Post-synthesis alumination has been extended to a new class of materials known as porous clay heterostructures (PCH) [46,47]. PCH are obtained by introducing a surfactant template into the interlayer region of clays (monmorillonites or saponites) and subsequently polymerizing a silica source around them to obtain a mesostructured silica framework within the clay inter-gallery region. Pinnavaia and co-workers [46] performed post-synthesis grafting of Al into the intragallery silica framework of a PCH precursor derived from a synthetic saponite clay. The resulting aluminated PCH materials exhibited basal spacings of 32–34.8 Å, surface areas of 623–906 m^2/g , pore volumes of 0.32–0.45 cm^3/g , and pore sizes in the 14–25 Å range. The Al content was determined by the Si/Al ratio of the alumination mixture. Nearly all of the grafted Al was

incorporated into tetrahedral sites in the intragallery silica framework. Sodium aluminate was found to be more effective (compared to aluminum chloride) for achieving higher loading of tetrahedral Al without forming (extra-framework) octahedral Al or collapsing the intercalated galleries. However the best retention of textural properties was achieved when the aluminations were carried out under acidic conditions using aqueous AlCl_3 as the aluminum source. On the other hand, Vansant *et al* [47] performed post-synthesis grafting of Al onto montmorillonite-PCH using an aluminium acetylacetonate complex as grafting reagent followed by a calcination step to anchor the Al. In this way, Brønsted acid sites, that were stable to thermal treatment at 300°C, were created.

4 Acidity and catalytic activity of Al-grafted mesoporous silicates

Early studies on Al-MCM-41 materials prepared by grafting Al onto pure silica MCM-41 [29-33] found that the materials exhibited considerable Brønsted acidity. An example is shown in Figure 7 [30]. The acid content in the Al-grafted MCM-41 materials was attributed to the presence of Brønsted acid generating Al in accessible sites on (rather than within) the pore walls [30,33]. The Al-grafted MCM-41 also possessed considerable catalytic activity for the cracking of cumene as shown in Figure 8 for ACH-grafted materials [33]. Chen and co-workers [36] prepared Al-MCM-41 materials via post-synthesis aluminations of pure silica MCM-41 using various Al sources, i.e., AlCl_3 , aluminum isopropoxide and sodium aluminate and compared their acidity to that of direct mixed-gel synthesised materials. The aluminated Al-MCM-41 had moderate acidity, comparable to that of the directly synthesized material. The acidity and catalytic activity of the aluminated materials are compared in Table 3. Dwyer *et al* [39] on the other hand investigated vapour phase aluminations of MCM-41. Over a similar range of Al content, the concentration of both Brønsted and Lewis acid sites (accessible to pyridine) was higher for the aluminated materials compared to directly prepared samples. This was reflected in catalytic activity, which was also higher for the post-synthesis aluminated MCM-41 materials [39].

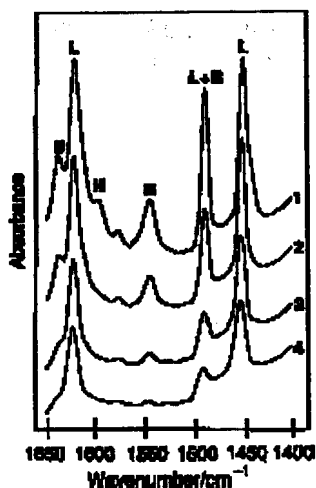


Figure 7. IR spectra of pyridine adsorbed on Al-grafted (using aluminium isopropoxide as Al source and hexane as solvent) MCM-41 (Si/Al = 6.1) following pyridine adsorption and thermal treatment at (1) 100°C, (2) 200°C, (3) 300°C and (4) 400°C. H denotes hydrogen-bonded pyridine; B Brønsted bound pyridine; L Lewis bound pyridine [30].

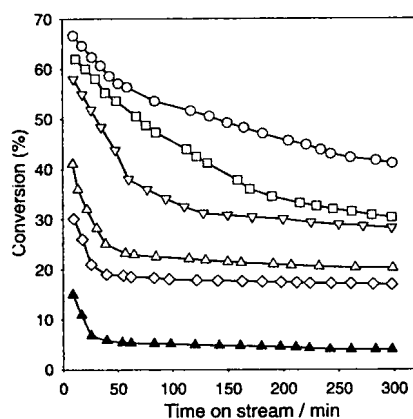


Figure 8. Deactivation behaviour during cumene conversion over Al-MCM samples and a reference material (ACH-grafted (0.24 mol l⁻¹) amorphous silica, AlSA, Si/Al = 9.9) at 300°C. AIMCM5, Si/Al = 6.1, (○); AIMCM4, Si/Al = 6.5, (□); AIMCM3, Si/Al = 7.4, (▽); AIMCM2, Si/Al = 9.8, (Δ); AIMCM1, Si/Al = 17.0, (◇) and AlSA (▲) [33].

Table 3. Acidity of various Al-containing MCM-41 samples and correlation with cumene activity at 300°C [36].

Sample no.	Si/Al	Bronsted acidity ($\mu\text{mol g}^{-1}$)	Lewis acidity ($\mu\text{mol g}^{-1}$)	Total acidity ($\mu\text{mol g}^{-1}$)	Cumene conv. (%)
Direct synthesis					
1	15.3	37.7	78.9	116.6	39.1
2	7.3	78.7	116.1	194.8	46.4
3	5.0	92.2	148.8	241.1	54.8
AlCl ₃ grafted					
6	6.4	79.6	117.8	197.4	40.9
7	4.9	69.9	119.8	189.7	33.8
8	1.3	30.8	132.4	163.2	25.4
Al-isopropoxide grafted					
9	11.8	0.5	28.6	28.6	2.5
10	3.3	5.6	100.8	106.4	33.1
11	1.3	64.5	95.7	160.4	41.8
NaAlO ₂ grafted					
12	3.2	78.1	93.8	171.9	49.7
Al(NO ₃) ₃ grafted					
13	62.7	28.6	88.5	117.1	19.5

The IR spectra of the pyridine adsorbed on TMA aluminated AlMCM-41 (Si/Al = 6.3) and protonated mordenite (MOR, Si/Al = 7.7) after evacuation at various temperatures is shown in Figure 9 [38]. The TMA aluminated MCM-41 was found by Sano and co-workers to have both Bronsted and Lewis acid sites [38]. The Bronsted acid sites of TMA aluminated MCM-41 were fewer and weaker than those of mordenite [38]. The catalytic activity of TMA aluminated MCM-41 was lower than that of mordenite and the rate of deactivation was also lower for the MCM-41 as shown in Figure 10. Sano and co-workers also compared the acidity and catalytic activity of Al-SBA-15 and Al-MCM-41 obtained via alumination with TMA [37]. Data from cumene cracking and pyridine adsorption experiments, shown in Figure 11 and 12, indicated that the Bronsted acid sites of Al-SBA-15 prepared via alumination with TMA were stronger than those of Al-MCM-41 prepared by the same method.

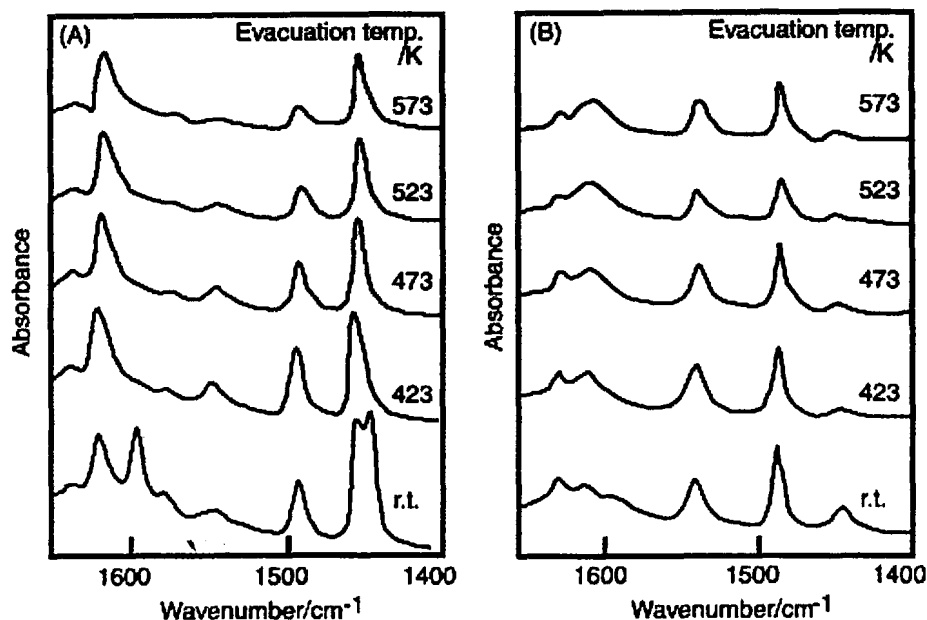


Figure 9. IR spectra of pyridine adsorbed on (A) TMA-grafted Al-MCM-41 (Si/Al = 6.3) and (B) mordenite (Si/Al = 7.7) at various evacuation temperatures [38].

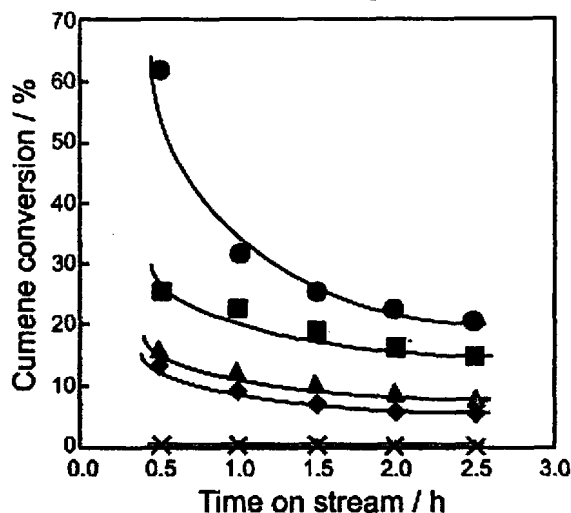


Figure 10. Conversion profiles of cumene on various TMA-grafted Al-MCM-41 samples and mordenite (Si/Al = 7.7). Reaction conditions: Temperature = 623 K, W/F = 0.20 h, (X) parent pure silica MCM-41; (◆) Al-MCM-41(1), Si/Al = 14.3; (▲) Al-MCM-41(2), Si/Al = 9.0; (■) Al-MCM-41(3), Si/Al = 6.3 and (●) mordenite [38].