Insertion of extra-framework Al into the framework of mesoporous MCM-41 aluminosilicates

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Virtually all octahedrally coordinated (extra-framework) Al in calcined Al-grafted MCM-41 materials can be inserted into (tetrahedral) framework positions upon treatment with an aqueous solution of NH₄OH; the insertion of Al into the framework is accompanied by an increase in (Brønsted) acidity and ion exchange capacity.

The recent synthesis of structurally well ordered mesoporous molecular sieves with uniform pores[1] has generated considerable research interest in the preparation and use of heteroatom containing mesoporous silicas as heterogeneous catalysts.[1,2] The incorporation of Al into mesoporous silicas is of particular interest as it gives rise to materials with solid acid and cation exchange properties. The acid and ion exchange sites are primarily associated with the presence of tetrahedrally coordinated Al in framework positions within the silica matrix. Al may be introduced into mesoporous silicas by direct synthesis[4,5] or by post-synthesis grafting methods.[6–8] Both methods, however tend to result in (calcined) materials with a significant proportion of extra-framework (octahedrally coordinated) Al.[4–8] It is desirable, with respect to acid catalysis and ion exchange properties, to maximise the proportion of Al in framework (tetrahedral) positions. So far no method has been described for modifying the siting of Al in calcined mesoporous aluminosilicates so as to maximise the amount (or proportion) of Al in framework positions. Reinsertion of extra-framework Al (EFAL) into framework positions has been previously described for dealuminated Y zeolites *via* hydrothermal treatment of the zeolite in an aqueous solution of KOH.[9] 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. Here we report a method *via* which virtually all octahedrally coordinated (extra-framework) Al in calcined Al-grafted MCM-41 materials can be inserted into (tetrahedral) framework positions. The method, which involves treatment of the mesoporous aluminosilicates with an aqueous solution of NH₄OH (pH ≈ 11.1), can be performed either at room temperature (30 °C) or at a range of temperatures up to 80 °C. NH₄OH was chosen due to the well known stability of Al-grafted MCM-41 materials at pH = 11,[10] and also because NH₄⁺ is potentially an acid generating cation (and therefore no further ion exchange would be required to maintain Brønsted acidity). Our findings show that insertion of EFAL into the framework increases the proportion of tetrahedrally coordinated Al and is accompanied by an increase in acidity and ion exchange capacity. Although the Al insertion method described here is generally applicable to any mesoporous aluminosilicates, this preliminary report concentrates on Al-grafted materials because they offer distinct advantages over directly synthesised materials with respect to accessibility to active (Al) sites, structural ordering and stability.[6–8,10–13]

The purely siliceous MCM-41 from which the Al-grafted materials were derived was prepared using normal procedures. The Al-grafted materials were prepared *via* two methods.[13] In the first method, 2.0 g of pure silica MCM-41 were dispersed in 50 ml dry hexane and added to 150 ml dry hexane containing the appropriate amount of aluminium isopropoxide to give a grafting gel Si/Al ratio of 5. The resulting mixture was stirred for 10 min and allowed to react at room temperature for 30 h. The obtained powder was filtered off, washed with dry hexane, dried at room temperature and calcined at 550 °C for 4 h. The resulting material with a bulk Si/Al ratio of 4.6 was designated CAP5.[13] In the second method, pure silica MCM-41 was added to a 50 ml solution of 0.48 mol l⁻¹ (w.r.t. Al) aluminium chlorhydrol at 80 °C and stirred for 2 h (at 80 °C). The resulting solid 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. To increase the amount of Al, the 'graft–wash–calcine' cycle was repeated once. The resulting material, designated CAH5, had a bulk Si/Al ratio of 4.7.[13] The calcined Al-grafted samples were then stirred in 1 M NH₄OH at a solution to solid ratio of 100 ml g⁻¹. At 30 °C, four 'stir–wash–dry' cycles were performed with each stirring lasting for 2 h. At 80 °C, the stirring was performed only once for 16 h. In both cases the NH₄OH-treated samples were thoroughly washed with distilled water and dried at 150 °C.

Fig. 1 shows the ²⁷Al MAS NMR spectra of CAP5 and CAH5 before and after treatment with NH₄OH. The untreated samples contain both tetrahedrally coordinated (δ 53) framework Al and octahedrally coordinated (δ 0) extra-framework Al. The proportion of tetrahedrally coordinated Al, calculated from the NMR spectra, is approximately 61% and 55% for CAP5 and CAH5 respectively. For both samples the proportion of tetrahedral Al increases significantly after treatment with NH₄OH. Indeed, after treatment with NH₄OH at 30 °C, virtually all (> 95%) of the Al is in tetrahedral coordination (Fig. 1b, e). Treatment in NH₄OH at 80 °C for 16 h appears to be slightly less effective in inserting the EFAL into framework positions probably due to its severity which affects structural integrity (see later). It is clear from Fig. 1 that the nature and environment of the Al in CAP5 and CAH5 is transformed by the relatively mild treatments in NH₄OH. Elemental analysis of the NH₄OH-
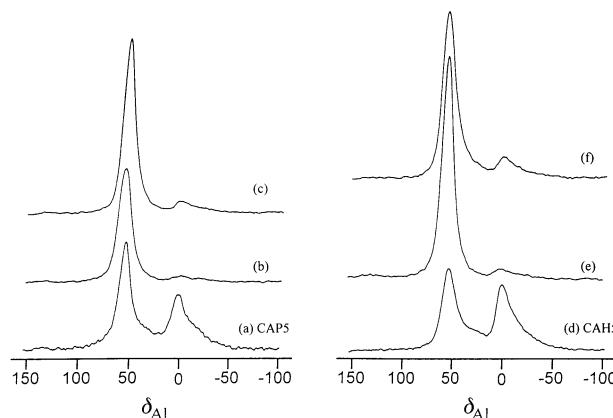

Fig. 1 ²⁷Al MAS NMR spectra of Al-grafted materials before and after treatment with NH₄OH; (a) CAP5, (b) CAP5 treated at 30 °C, (c) CAP5 treated at 80 °C, (d) CAH5, (e) CAH5 treated at 30 °C and (f) CAH5 treated at 80 °C.

Table 1 Elemental composition, textural properties and acidity of the studied materials

Sample	Si/Al	Surface area/ $m^2 g^{-1}$	Pore volume/ $cm^3 g^{-1}$	Acidity/mmol $H^+ g^{-1}$
CAP5	4.6	791	0.74	0.81
30 °C[a]	4.9	728	0.67	1.15
80 °C[a]	4.8	428	0.45	1.09
CAH5	4.7	740	0.52	0.95
30 °C[b]	4.9	620	0.55	1.16
80 °C[b]	4.3	490	0.36	1.11

[a] CAP5 treated with NH_4OH at the temperature shown. [b] CAH5 treated with NH_4OH at the temperature shown.
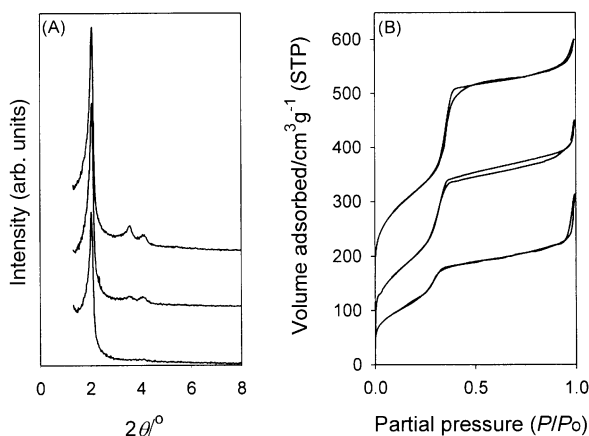
Fig. 2 Powder XRD patterns (A) and nitrogen sorption isotherms (B) of CAP5 before and after treatment with NH_4OH; CAP5 (top), CAP5 treated at 30 °C (middle) and CAP5 treated at 80 °C (bottom).

treated samples was performed in order to find out whether any preferential leaching of Si or Al occurred during the treatments. The Si/Al ratios of the NH_4OH-treated samples are given in Table 1. In all cases the elemental composition remained unchanged, *i.e.*, all the Si and Al was retained during NH_4OH treatment. This indicates that the increase in the tetrahedral/octahedral Al ratio observed from the MAS NMR spectra was due to insertion of EFAl into the framework rather than preferential dissolution of octahedral Al.

The acid contents of the Al-grafted samples and their NH_4OH-treated analogues are given in Table 1. The acid content was determined using thermally programmed desorption of cyclohexylamine.[13] Prior to analysis, the base (cyclohexylamine) containing samples were heated at 80 °C for 2 h. The acidity data indicate that an increase in the proportion of tetrahedral Al following NH_4OH treatment is accompanied by an increase in acid content. The increase is particularly remarkable for CAP5. Since the elemental composition remained unchanged (*i.e.* the amount of Al per gram of sample remained the same), the only explanation for the increased acidity is insertion of EFAL into acid generating framework sites. The insertion of EFAL into the framework is expected to specifically increase the proportion of Brønsted acid sites. Indeed, using FTIR spectroscopy of adsorbed pyridine (see ref. 17 for details) we observed a significant increase in the Brønsted acid content of NH_4OH-treated samples. For example, after evacuation at 100 °C,[14] the Brønsted acid content of CAH5 increased from 34 to 72 µmol g^{-1} and the Brønsted/Lewis acid ratio increased from 0.27 to 0.58. The same trend was observed after evacuation at 200 and 300 °C.[14] Furthermore, a preliminary check on ion exchange properties indicated that NH_4OH-treated samples exhibit substantially higher cation exchange capacities compared to the untreated samples; M^+/Al ratios of the Al-grafted materials (obtained following ion exchange) increased from *ca.* 0.4 to as high as 0.9 after treatment with

NH_4OH at 30 °C. We were also able to observe Brønsted acid bridging OH groups in the FTIR spectra of NH_4OH-treated samples. These observations clearly point to the insertion of EFAL into framework positions rather than the formation of a separate alumina phase in which the Al is tetrahedrally coordinated.

The XRD patterns and sorption isotherms (obtained using a Coulter SA3100 Sorptometer after evacuating overnight at 200 °C) for CAP5 and its NH_4OH-treated analogues are shown in Fig. 2A. The insertion of Al into the framework (especially at 30 °C) does not appear to be detrimental to the structural ordering. CAP5 treated at 30 °C exhibits an XRD pattern and sorption isotherm comparable to that of the parent material. We note that CAP5 treated at 30 °C is very well ordered for an MCM-41 material with such a low (*ca.* 4.9) framework Si/Al ratio. Treatment at 80 °C results in rather more structural degradation; however, the resulting material still retains some hexagonal ordering and mesopore uniformity. The greater structural degradation for the 80 °C treated CAP5 may be the cause of the slightly less efficient insertion of Al into the framework observed from the MAS NMR spectra in Fig. 1. Table 1 shows the textural properties for the Al-grafted materials and their NH_4OH treated analogues. In general Al insertion results in a decrease in the surface area and pore volume. The decrease is modest at 30 °C but greater for materials treated at 80 °C. Note, however, that the effects of 80 °C NH_4OH treatment are reported here as an upper limit (with respect to severity of the treatment) and to show the versatility of the insertion method.

The mechanism for Al insertion most likely involves the dissolution of EFAL and the formation of aluminate ions that are inserted into the framework.[9] This is possible due to the amorphous nature of the pore walls and the presence of silanols (which may act as anchoring sites) on the pore wall surfaces. The pH of the basic solution used is important; a strongly basic solution dissolves both the EFAL and the mesoporous framework while a mildly basic solution does not dissolve the EFAL and is therefore not effective in Al insertion. Indeed when the strongly basic KOH solution (pH = 13.5) was used, the Al-grafted materials were destroyed. On the other hand, Al-grafted materials treated with KNO_3 (pH ≈ 8.8) remained virtually unchanged; neither structural ordering nor Al siting was affected. It appears therefore that NH_4OH (pH ≈ 11.1) is just right with respect to both the dissolution (and insertion) of EFAL into the framework and the preservation of structural integrity of the mesoporous framework. At the moment we have no evidence that the nature of the cation affects the insertion process.

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