Aluminosilicate mesoporous molecular sieves with enhanced stability obtained by reacting MCM-41 with aluminium chlorohydrate

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Aluminosilicate MCM-41 materials prepared by post-synthesis alumination using aqueous aluminium chlorohydrate exhibit remarkably high mechanical and hydrothermal stability and in addition the materials, after steaming at high temperatures, possess stronger Brønsted acid sites compared to the parent material.

Recently, heteroatom substituted mesoporous molecular sieves such as MCM-41 have attracted much interest due to their potential use as hosts, adsorbents or catalysts.[1] Of particular interest are Al-containing materials which may be used as solid acid catalysts.[2,3] The structural stability of such aluminosilicate mesoporous molecular sieves is very important to their application as catalysts. Indeed the thermal and hydrothermal stability of Al-containing MCM-41 has been the focus of much recent research.[3,4] Despite good thermal stability, AlMCM-41 materials generally suffer from poor (and unpredictable) structural ordering and low hydrothermal stability and are easily destroyed by boiling in water or by steaming at high temperatures.[3,4] Studies on the mechanical stability of mesoporous molecular sieves have concentrated on pure silica materials[5] and to the best of our knowledge there is no data on the mechanical stability of silica-alumina materials. The structural stability of mesoporous molecular sieves can be improved by increasing the thickness of the pore walls and/or by enhancing the local ordering of the walls. This may be achieved by post-synthesis treatments such as pore wall grafting[6] or recrystallisation.[7] We have recently discovered that structurally well ordered AlMCM-41 can be prepared by reacting purely siliceous MCM-41 with aluminium chlorohydrate (ACH) solution containing Al polycations. Herein we report on the remarkable stability of the resulting aluminosilicate materials.

The starting material, a purely siliceous MCM-41 (designated PSMCM), was prepared according to ref. 8. AlMCM-41 was prepared by adding 1.0 g of calcined PSMCM to a 50 ml solution of ACH at 80 °C and stirring for 2 h (at 80 °C). 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. The physical properties of the purely siliceous material (PSMCM) and AlMCM-41 samples prepared from ACH solutions with Al concentrations of 0.12, 0.30 and 0.48 mol l^{-1} (designated AlMCM2 (Si/Al = 9.7), AlMCM4 (Si/Al = 6.5) and AlMCM5 (Si/Al = 6.1) respectively) are given in Table 1. The *d* spacing of the AlMCM materials is higher than that of the starting PSMCM material and generally increases with the amount of aluminium incorporated. This is consistent with the incorporation of increasing amounts tetrahedral Al into the framework and is in part due to the longer Al–O bond length compared to the Si–O bond. The effect of the incorporation of Al onto the framework is clearly illustrated by the changes in the thickness (calculated by subtracting the pore diameter from the lattice parameter) of the pore walls. At 16 Å the wall thickness of PSMCM is comparable to the largest reported values for MCM-41.[8] On Al incorporation the wall thickness progressively increases up to 23.9 Å (for AlMCM5). 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. The surface area reduces slightly while the pore volume shows a larger decrease. However, the lowest surface area (753 $m^2\ g^{-1}$) and pore volume (0.62 $cm^3\ g^{-1}$) obtained for the most aluminous sample (AlMCM5) is still high.

The mechanical stability of the Al-grafted materials was investigated by pressing the materials in a steel die of diameter 13 mm for 10 min. The effects of compression (external pressures were calculated from the applied force and the die diameter) on the ordering and textural properties of AlMCM4 (Si/Al = 6.5) are shown in Fig. 1 and Table 1. Except for a slight decrease in the *d* spacing, compaction at 185 MPa does not have any significant effect on the XRD pattern of AlMCM4. The retention of structural integrity is confirmed by the minimal decrease in the surface area and pore volume (Table 1). Compaction at 370 MPa resulted in a decrease in XRD peak intensity (with no further decrease in *d* spacing) and was accompanied by a 29% decrease in surface area and 25% decrease in pore volume. After compaction at the higher pressure of 740 MPa the surface area and pore volume reduced by 60%. However, the XRD pattern still indicates retention of some hexagonal symmetry. The mechanical stability exhibited here is remarkable especially in the light of previous studies which have shown that pure silica MCM-41 is essentially destroyed at 224 MPa.[5] It is likely that the stability observed

Table 1 *d* spacing and textural properties of the studied 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
AlMCM2	42.0	760	0.69	29.3	48.5	19.2
AlMCM4	42.8	767	0.65	26.5	49.4	22.9
AlMCM4 (185 MPa)[c]		755	0.57	27.4		
AlMCM4 (370 MPa))[c]		547	0.49	28.5		
AlMCM4 (740 MPa))[c]		284	0.26	30.6		
AlMCM5	43.0	753	0.62	25.8	49.7	23.9
ST-AlMCM5)[d]		558	0.45	22.6		
REF-AlMCM5)[e]		834	0.70	24.9		

[a] APD = average pore diameter (determined using BJH analysis). [b] a_0 = Lattice parameter, from the XRD data using the formula $a_0 = 2d_{100}/\ 3$. [c] Sample AlMCM4 compressed at the pressures shown in parentheses. [d] Sample AlMCM5 steamed at 750 °C for 4 h. [e] Sample AlMCM5 refluxed in distilled water for 16 h.

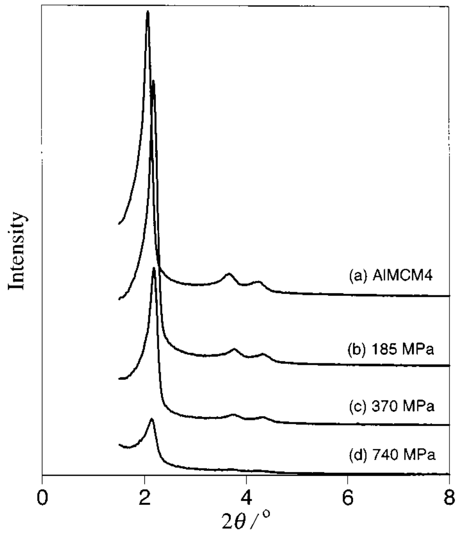

Fig. 1 Powder XRD patterns of sample AlMCM4; (a) original material and after compaction at (b) 185 MPa, (c) 370 MPa and (d) 740 MPa

here is due to the much thicker walls of the Al-grafted sample; a direct (mixed-gel) synthesised Al-MCM-41 material (with a Si/Al ratio of 23 and 11 Å thick walls) was destroyed after compaction at 370 MPa. We also investigated the mechanical stability of the pure silica starting material (PSMCM) and observed good structural integrity (not unlike that of AlMCM4) up to 370 MPa. However, after compaction at 740 MPa the degradation of PSMCM (as indicated by XRD) was much greater than that of AlMCM4.

To investigate hydrothermal stability, the Al-grafted materials were subjected to steaming at 750 °C for 4 h or refluxing in distilled water for 16 h (at a water to sample ratio of 1 l g^{-1}). The effects of these treatments on the ordering and textural properties of AlMCM5 (Si/A/ = 6.1) are shown in Fig. 2 and Table 1. After steaming, the Al-grafted sample exhibits an XRD pattern which indicates retention of structural ordering albeit with reduced peak intensity and lower *d* spacing. This is accompanied by a 3.2 Å reduction in pore diameter and a 25% decrease in both the surface area and pore volume. Previous studies have shown that whereas pure silica MCM-41 is relatively stable to steaming, Al-containing MCM-41 materials are on the other hand highly unstable.[3] It is therefore noteworthy that the Al-grafted material reported here is able to maintain structural ordering and considerably high surface area and pore volume. To ascertain the effect of steaming on catalytic properties we compared the acid content[2] and activity (for cumene cracking)[2] of AlMCM5 with its steamed analogue (ST-AlMCM5). The acid content of ST-AlMCM5 was 0.257 mmol $H^+ g^{-1}$ compared to 0.605 mmol $H^+ g^{-1}$ for AlMCM5. However, despite a lower acid content, the conversion of cumene was higher for the steamed sample; ST-AlMCM5 had an initial rate (in mmo l g^{-1} h^{-1} and taken at 10 min time on stream) of 1.225 compared to a rate of 0.843 for AlMCM5. This translates to an apparent turnover frequency (TOF) of 4.75 over ST-AlMCM5 and 1.4 over AlMCM5. This results indicate that the acid sites in the steamed sample (though fewer in number due to some dealumination) are stronger than those on AlMCM5. This observations are reminiscent of the behaviour of steam stabilised Y zeolites. To the best of our knowledge, this is the first example of an Al-containing MCM-41 material, which exhibits such stability to high temperature steaming. Indeed a direct (mixed-gel) synthesised Al-MCM-41 material (Si/Al = 23) was destroyed by similar hydrothermal treatment with its surface area decreasing by 75%.

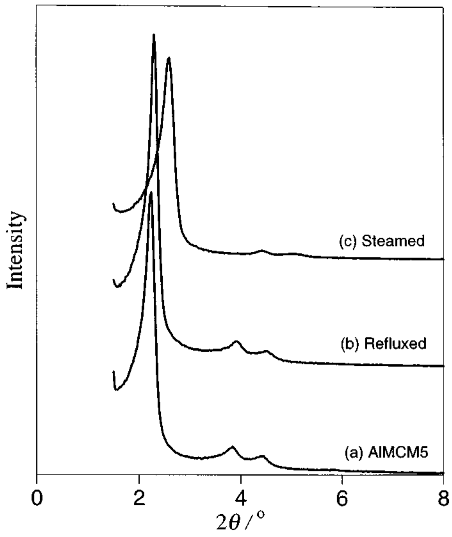

Fig. 2 Powder XRD patterns of sample AlMCM5; (a) original material and after (b) refluxing in water for 16 h and (c) steaming at 750 °C for 4 h

The hydrothermal stability of the Al-grafted materials is further illustrated by their stability in boiling water. Fig. 2 indicates that heating (refluxing) of AlMCM5 in boiling water for 16 h had virtually no deleterious effect on its XRD pattern which suggests excellent retention of structural ordering. This is confirmed by the fact that the surface area and pore volume, far from decreasing, actually increase (Table 1). When subjected to similar treatment the structural ordering of the pure silica starting material (PSMCM) was destroyed and its surface area reduced by 65%. The direct (mixed-gel) synthesised Al-MCM-41 material (Si/Al = 23) was even less stable and was rendered amorphous after refluxing in water for a shorter time of 6 h.

We have demonstrated that Al-containing MCM-41 with good structural stability can be prepared by reacting purely siliceous MCM-41 with aluminium chlorohydrate. The enhanced mechanical and hydrothermal stability of materials reported here may be due to recrystallisation effects, involving the grafted Al, which act to heal defect sites in the structure of the MCM-41 materials. This is likely because the Al is initially grafted onto the pure silica material *via* silanol groups which are known to occur at defect sites. Similar recrystallisation effects are known to occur in zeolites.[9] Stable aluminosilicate MCM-41 materials are expected to find use as solid acid catalysts especially for processes which require catalyst regeneration under severe conditions.

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Notes and References

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