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Influence of pore wall thickness on the steam stability of Al-grafted MCM-41

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Mesoporous aluminosilicate MCM-41 with improved steam stability may be prepared by grafting Al onto pure silica MCM-41 materials that possess thick pore walls.

Mesostructured aluminosilicates are currently attracting considerable research interest due to their potential use as heterogeneous catalyst.[1,2] Their main attraction is a well ordered mesostructure with uniform pores whose size is much larger than that of channels present in traditional microporous zeolites. They are therefore able to catalyse chemical transformations involving molecules too large to fit the pore channels of zeolites. The use of mesoporous aluminosilicates such as Al-MCM-41, in for example the cracking of heavy fractions in petroleum refining, is however hampered by their inadequate hydrothermal stability, which is lower than that of zeolites.[1,3] There have been several recent studies aimed at improving the hydrothermal stability of mesoporous aluminosilicates in boiling water and/or under steaming conditions.[4–7] It has been shown that Al-MCM-41 materials prepared *via* grafting routes are extremely stable in boiling water.[4–6] Directly prepared Al-MCM-41 has also been shown to exhibit considerable hydrothermal stability especially at relatively low Al contents.[8,9] More recently Liu *et al.* have shown that steam stable mesostructured aluminosilicates may be prepared using zeolite type seeds.[7] It has recently been suggested that a possible route to steam stable Al-MCM-41 is *via* the preparation of materials with thick pore walls.[1,3] However an attempt to prepare such steam stable (thick walled) Al-MCM-41 *via* direct (mixed-gel) synthesis was unsuccessful.[1,3] The direct mixed gel synthesis of Al-MCM-41 is known to be unpredictable and therefore it is to be expected that any attempt to carefully control the pore wall thickness will present considerable challenges. The pore wall thickness of pure silica MCM-41 can, on the other hand, be readily controlled by careful choice of synthesis conditions.[10,11] Here we report on the influence of pore wall thickness on the steam stability of Al-grafted MCM-41 and show that the stability of these materials can be remarkably improved by using thick-walled pure silica MCM-41 as ‘starting material’. The improvement in structural steam stability is accompanied by a higher retention of acidity which is important for the use of these materials as solid acid catalysts. Mesostructured aluminosilicates prepared *via* grafting routes offer distinct advantages over directly synthesised materials with respect to accessibility to active (Al) sites and structural ordering;[12] their stabilisation is therefore desirable. Furthermore their preparation is not restricted by ‘template synthesis’ which can be expensive, irreproducible and in some cases inimical to the incorporation of Al. The starting point for Al-grafted materials is the purely siliceous mesoporous silica, which may take any form (hexagonal, cubic, lamellar) and can be prepared *via* a range of inexpensive synthesis routes employing cationic, neutral, non-ionic or even non-surfactant templates and cheap sources of silica.[13]

In order to vary the pore wall thickness of the starting pure silica MCM-41 materials, three different crystallisation regimes were used. This was achieved by varying the crystallisation temperature and duration. In brief the three purely siliceous MCM-41 materials were prepared by dissolving tetramethylammonium hydroxide (TMAOH) and cetyltrimethyammonium bromide (CTAB) in distilled water by stirring at 35 °C. The silica source, fumed silica (sigma), was then added to the solution under stirring for 1 h. After further stirring for 1 h the resulting synthesis 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 as follows; at 150 °C for 48 h (standard Si-MCM-41, designated sample A),[9] 140 °C for 96 h (sample B) and 145 °C for 96 h (sample C). In each case the solid product was obtained by filtration, washed with distilled water, dried at room temperature and calcined in air at 550 °C for 8 h. Al-grafted MCM-41 materials were prepared at a target bulk Si/Al ratio of 13 as previously described using aluminium chlorhydrol as the grafting reagent.[14] In all cases the final bulk Si/Al ratio was very close to the expected value and the proportion of tetrahedrally coordinated Al was similar. The Al-grafted samples were designated Al-MCM41-A, Al-MCM41-B and Al-MCM41-C where A, B and C represent the pure silica MCM-41 material from which they were derived. Hydrothermal stability was tested by heat treatment at 800 or 900 °C for 4 h in a flow of nitrogen saturated with water vapour at room temperature.

The textural parameters of the Al-grafted materials before and after hydrothermal treatment are given in Table 1. The basal spacing increases from sample Al-MCM41-A to Al-MCM41-C; this is consistent with previous results, which show that crystallisation at higher temperature and/or longer time favours larger basal spacing.[10,11] The surface area decreases from sample Al-MCM41-A to Al-MCM41-C while the pore volume remains constant. This is accompanied by an increase in pore size and pore wall thickness as shown in Table 2. The data in Table 2 is calculated using two methods, so as to clearly demonstrate the variation in pore wall thickness. Powder XRD and N_2 sorption isotherms obtained for the Al-grafted materials before hydrothermal treatment are given in Figs. 1 and 2 respectively. In all three cases well ordered aluminosilicate materials were obtained as indicated by the XRD patterns. All the samples also exhibit a N_2 sorption isotherm with a well developed step in the relative pressure (P/P_o) range 0.2–0.5 characteristic of capillary condensation into uniform mesopores.

Figs. 1 and 2 show the powder XRD patterns and N_2 sorption isotherms of the Al-grafted materials after hydrothermal treatment at 800 and 900 °C for 4 h. All the samples are

Table 1 Textural properties and acidity of the studied materials

Sample	d_{100}/Å	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Acidity/ mmol H^+ g^{-1}
Al-MCM41-A	42.2	907	0.78	0.83
steamed 800 °C	39.4	785	0.58	0.41
steamed 900 °C	35.0	224	0.19	0.16
Al-MCM41-B	50.7	749	0.76	0.82
steamed 800 °C	47.3	674	0.64	0.48
steamed 900 °C	41.8	258	0.27	0.18
Al-MCM41-C	55.6	734	0.78	0.84
steamed 800 °C	51.4	727	0.88[a]	0.71
steamed 900 °C	45.7	501	0.48	0.40

[a] Includes some textural mesoporosity.

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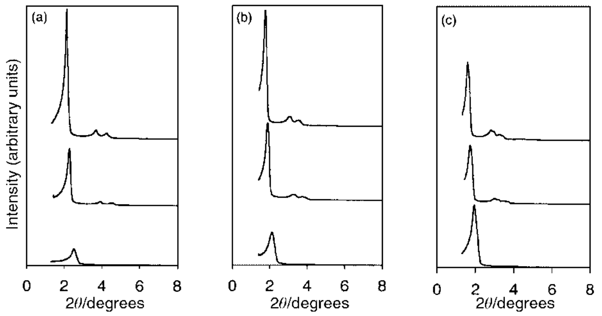

Fig. 1 Powder XRD patterns of Al-grafted MCM-41 samples, (a) Al-MCM41-A, (b) Al-MCM41-B and (c) Al-MCM41-C, before (top) and after hydrothermal treatment at 800 °C (middle) and 900 °C (bottom). The intensity scale is the same for all samples.

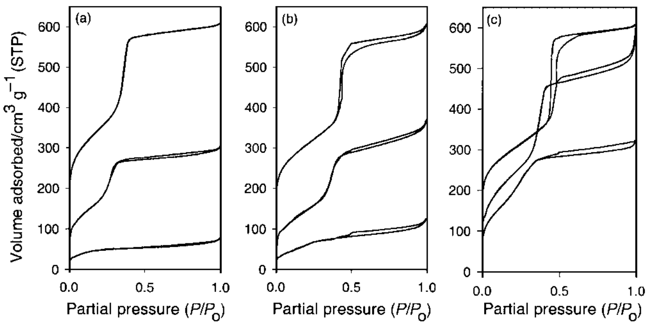

Fig. 2 Nitrogen sorption isotherms of Al-grafted MCM-41 samples, (a) Al-MCM41-A, (b) Al-MCM41-B and (c) Al-MCM41-C, before (top) and after hydrothermal treatment at 800 °C (middle) and 900 °C (bottom).

Table 2 Comparison of pore diameter and corresponding pore wall thickness for Al-grafted materials

	Pore diameter/Å			Wall thickness/Å	
Sample model	a_o	$4V/S$	Geometric model[a]	$4V/S$	Geometric model[a]
Al-MCM41-A	48.7	34.4	38.1	14.3	10.6
Al-MCM41-B	58.5	40.6	45.6	17.9	12.9
Al-MCM41-C	64.2	42.5	50.2	21.7	14.0

[a] Pore diameter (PD) was calculated based on a geometric model according to the equation:[16] $PD = cd(\rho V_p/1 + \rho V_p)^{1/2}$, where $c = 1.213$, ρ (density of silica walls) = 1.6 g cm^{-3},[17] and d is basal spacing (d_{100}) and V_p is mesopore volume; a_o = the lattice parameter from the d_{100} spacing using the formula $a_o = 2d_{100}/\sqrt{3}$; wall thickness = a_o − PD.

relatively stable at 800 °C. The decrease in pore volume after treatment at 800 °C is 26% for sample Al-MCM41-A and 16% for sample Al-MCM41-B. In contrast the mesopore volume of sample Al-MCM41-C remains virtually unchanged while its total pore volume increases due to the presence of textural mesoporosity. The surface area follows the same trend. These observations imply that hydrothermal stability at 800 °C is, to some extent, influenced by the pore wall thickness. The influence of pore wall thickness is more clearly illustrated after the more severe hydrothermal treatment at 900 °C. From Fig. 1 and 2 it is clear that sample Al-MCM41-A, which has the thinnest pore walls, is severely degraded after treatment at 900 °C. The N_2 sorption isotherm of the resulting material exhibits virtually no mesoporous character. The surface area and pore volume decrease by 75%. Sample Al-MCM41-B shows better retention of structural ordering after treatment at 900 °C compared to sample Al-MCM41-A; its surface area and pore volume are reduced by *ca.* 65% although it still exhibits a N_2 sorption isotherm with some mesoporous character. When subjected to similar treatment, sample Al-MCM41-C shows considerable retention of structural ordering; the XRD pattern of Al-MCM41-C steamed at 900 °C is comparable to that of the parent material and its N_2 sorption isotherm still exhibits a relatively sharp mesopore filling step. The surface area and pore volume are reduced by only 32 and 38% respectively. It appears therefore that the steam stability of the Al-grafted MCM-41 materials increases with increasing pore wall thickness. It is worth pointing out that the steam stability of the pure silica 'starting' samples was very poor (in any case lower than that of the Al-grafted materials) and increased only marginally with increasing pore wall thickness. The surface area of pure silica samples A, B and C, after steam treatment at 900 °C for 4 h, was 69, 105 and 150 m^2 g^{-1} while the pore volume was 0.12, 0.15 and 0.21 cm^3 g^{-1}, respectively. The improved stability exhibited by the Al-grafted samples with thicker pore walls is therefore due to a combination of the strengthened framework and the presence of Al in the framework.[15] On stability of the core silica framework, we further note that the extent of silica condensation in the as-synthesised pure silica samples increased with pore wall thickness.[10] Consequently on calcination, the more polymerised (thicker walled) samples undergo less 'forced' condensation thus resulting in fewer strained siloxane bonds within the core silica framework. The greater stability of the thicker walled Al-grafted samples is accompanied by better retention of acidity as indicated by the data (determined using thermally programmed desorption of cyclohexylamine as previously described[4]) in Table 1. In brief samples saturated with cyclohexylamine (CHA) were pre-treated at 80 °C for 2 h and cooled under nitrogen prior to thermogravimetric analysis.[4] The weight loss between 300 and 450 °C was used to compute the acid content in mmol CHA g^{-1} assuming that each base molecule interacts with one acid site. Better retention of acidity may be an indication of lower levels of dealumination in the thicker walled Al-grafted samples. The findings reported here open new opportunities for the preparation of steam stable Al-MCM41 given that there are other methods that can be used to stabilise the pure silica starting material prior to Al grafting.

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