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Template-directed stepwise post-synthesis alumination of MCM-41 mesoporous silica

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Stepwise post-synthesis alumination of pure silica MCM-41 in which increasing proportions of the MCM-41 are aluminated depending on the amount of Al available in the synthesis gel is achieved during secondary synthesis (*i.e.* recrystallisation) of calcined pure silica MCM-41 in the presence of discrete amounts of Al.

The recent synthesis of MCM-41 type mesoporous silicas which possess well ordered pores of diameter 20–100 Å has expanded the range of heterogeneous catalysis into the mesoporous regime.[1–4] With regard to catalysis, purely siliceous mesoporous molecular sieves are of limited use owing to the absence of active sites in their matrices. Active sites may be generated *via* chemical modification involving the introduction of heteroatoms into the silica matrix.[2–4] The incorporation of Al (which gives rise to solid acid catalysts with acid sites associated with the presence of Al in framework positions) is a typical example. The introduction of Al into mesoporous silicas (*i.e.* alumination) normally takes place in a homogeneous form and results in uniform incorporation of Al with little control of its spatial distribution. Increasing the Al content in the synthesis gel generally results in a uniform increase in the amount of incorporated Al throughout the entire sample.[5] In a departure from this norm, this report describes preliminary work on the unusual stepwise post-synthesis alumination of pure silica MCM-41 in which increasing proportions of the MCM-41 are aluminated depending on the amount of Al available in the synthesis gel. This apparently step-wise alumination is achieved during secondary synthesis (recrystallisation) of calcined pure silica MCM-41 in the presence of discrete amounts of Al. Evidence from several characterisation techniques indicates that during recrystallisation, the proportion of aluminated MCM-41 increases 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 is aluminated. The findings reported here suggest that it is possible to fully aluminate a portion of the pores of a pure silica MCM-41 before alumination of other pores has started, resulting in an apparently mixed-phase material. The ability to vary the spatial distribution of Al (or other heteroatoms) in such a manner may find use in the preparation of composite or multiphase materials and may open new opportunities for selective molecular engineering within the internal surface of mesoporous silicas.

We have recently shown that calcined pure silica MCM-41 is stable under normal MCM-41 synthesis conditions and that when used as the ‘silica source’ during secondary synthesis (*i.e.* recrystallisation) the calcined MCM-41 crystallites are preserved and act as seeds for further crystal enlargement.[6,7] This ‘preservation’ principle was used to prepare a series of recrystallised Al-MCM-41 samples by adding varying amounts of Al to the recrystallisation gel. The recrystallised samples were prepared as previously described[6,7] except that aluminium isopropoxide was added to the recrystallisation gel along with the calcined pure silica MCM-41 at gel Si/Al ratios in the range 5–80. In brief, tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water by stirring at 35 °C. Calcined pure silica MCM-41 and the required amount of Al (as aluminium isopropoxide) were then added to the template solution under stirring for 1 h. After further stirring for 1 h the resulting gel was aged for 20 h at room temperature and then 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. The samples were designated Al-MCM41-*x*, where *x* is the gel Si/Al ratio.

Powder X-ray diffraction (XRD) patterns of the parent pure silica MCM-41 and the aluminated samples are shown in Fig. 1. The XRD pattern of the parent Si-MCM-41 material exhibits a single (100) basal peak and several higher order peaks which is typical of a well ordered MCM-41. The XRD patterns of aluminated materials prepared at gel Si/Al ratios of 80, 40 and 20 exhibit two low angle peaks; the original 100 peak and a new peak which occurs at slightly higher 2θ values and progressively shifts to even higher values (*i.e.* lower basal spacing) as the gel Si/Al ratios reduced from 80 to 20. Furthermore the intensity of the new peak increases at the expense of the original basal peak. The position of the original peak does not however change despite the reduction in intensity (Table 1). At a gel Si/Al ratio of $\leqslant 10$, the original basal peak is completely lost and only the new peak is observed. Our preliminary interpretation of the XRD results is that the new peak is due to aluminated MCM-41 which increases in proportion as the amount of Al in the recrystallisation gel increases and that at a gel Si/Al ratio close to 10, the whole sample is aluminated and therefore only the new peak is observed. The presence of the original peak for samples recrystallised at a Si/Al gel ratio of 80, 40 and 20 implies that a portion of these samples remains essentially non-aluminated and retains the characteristics of the parent Si-MCM-41 material. This interpretation is consistent with the fact that in the absence of Al (*i.e.* in all silica recrystallisation) only one peak (*i.e.* the original peak) is observed,[6] which supports our proposal that the new peak observed here is due to the presence of Al. Our interpretation of the XRD results is

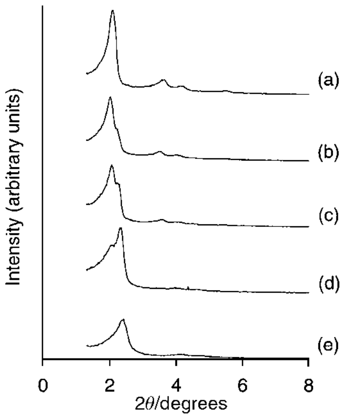

Fig. 1 Powder XRD patterns of pure silica Si-MCM-41 (a) and recrystallised Al-MCM41-80 (b), Al-MCM41-40 (c), Al-MCM41-20 (d) and Al-MCM41-10 (e) materials.

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Table 1 Textural properties of the studied materials

Sample	Basal (d_{100}) spacing/Å	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}
Si-MCM-41	42.8	1017	0.91
Al-MCM41-80	43.2; 40.1	995	0.87
Al-MCM41-40	43.0; 39.7	922	0.78
Al-MCM41-20	42.8; 38.2	840	0.62
Al-MCM41-10	37.6	785	0.53
Al-MCM41-5	33.5	878	0.51

supported by the N_2 sorption isotherms in Fig. 2 which clearly show two capillary condensation (pore filling) steps for the 'partially' aluminated samples (Al-MCM41-80, Al-MCM41-40 and Al-MCM41-20). The first step (at lower partial pressure) is ascribed to the filling of aluminated pores and the second step to the filling of non-aluminated pores. It is noteworthy that the second pore filling step in the 'partially' aluminated samples occurs at the same partial pressure as the filling of pores in the parent Si-MCM-41. This indicates that the pore size of the channels in the parent sample remains unchanged in the 'partially' aluminated samples.

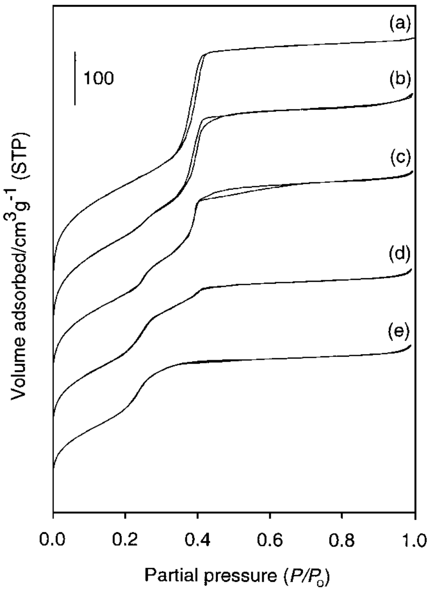

Fig. 2 Nitrogen sorption isotherms of pure silica Si-MCM-41 (a) and recrystallised Al-MCM41-80 (b), Al-MCM41-40 (c), Al-MCM41-20 (d) and Al-MCM41-10 (e) materials.

The coexistence of the two distinct pore systems within one sample implies that alumination of a portion of pores is accomplished before the start of alumination in other pores. The reduction in basal spacing and pore size (Fig. 1 and 2) and the gradual decrease in surface area and pore volume (Table 1) which accompanies the alumination is consistent with the incorporation of an aluminosilicate layer on the inner pore walls of the parent Si-MCM-41. The incorporation of Al onto the silica framework must be accompanied by charge balancing surfactant molecules since there are no inorganic ions present in the recrystallisation gel. It is likely that the strong interaction between the charge balancing surfactant molecules and the framework Al sites causes contraction of the mesoporous framework, resulting in a reduced basal spacing in the aluminated parts of the recrystallised sample. Indeed thermogravimetric analysis (TGA) of as-synthesised samples indicated the presence of strongly held surfactant molecules (associated with framework Al) whose proportion increased with the extent of alumination. Incorporation of Al onto the framework was confirmed by ^{27}Al MAS NMR of the calcined samples. More than 80% of the Al in the samples (except for Al-MCM41-5 with 65%) was found to be in tetrahedral coordination. During recrystallisation, the surfactant molecules and Al which are eventually occluded/incorporated into the recrystallised Al-MCM-41 samples must be transported into the pores of existing Si-MCM-41 particles/crystallites.[6,7] We propose that the transportation of Al into the pores is, owing to the presence of the surfactant, diffusion controlled and that the Al is therefore first incorporated into the outer region of the MCM-41 particles. Alumination then proceeds into the interior of the sample depending on the amount of Al available. If all the particles are equally accessible, then each particle is aluminated from the edges inwards until all the Al is depleted or in an aggregate of particles, the outermost particles are aluminated first while the inner particles remain untouched by the Al. In such a scenario, the proportion of aluminated MCM-41 will depend on the amount of Al available and the diffusion time. In the present study the diffusion time (*i.e.* synthesis time) was kept constant and the only variable was the amount of Al. For the partially aluminated samples, SEM with elemental analysis gave Si/Al ratios of 40.1, 28.3 and 16.9 for Al-MCM41-80, Al-MCM41-40 and Al-MCM-41-20, respectively. The implied Al content for these samples was higher than that expected from the gel Si/Al ratio which is not suprising considering that only part of the pure silica MCM-41 is aluminated. It is also evident that the Si/Al ratio approaches the expected value as the extent of alumination increases. Indeed at full alumination (gel ratio Si/Al 10 and 5) the obtained elemental composition (Si/Al = 8.8 for Al-MCM-41-10 and 5.8 for Al-MCM41-5) is very close to the expected values since the samples are essentially homogeneous with respect to spatial distribution of Al. The alumination mechanism proposed here is similar to that suggested by Anwander *et al.* for the chemisorption of trimethyaluminium into MCM-41.[8] We also note that the incorporation of Al predominantly into the outer region of MCM-41 was previously observed when Al was added to an already formed surfactant–silicate mesostructure.[9]

We have considered other scenarios that are possible during the recrystallisation; (i) the parent Si-MCM-41 can completely dissolve to generate silicate ions which then interact with the Al. This would in effect be equivalent to conventional direct mixed-gel synthesis and should yield homogeneous Al-MCM-41 materials with uniform pores and elemental compositions close to the gel Si/Al ratio irrespective of the amount of Al.[5,10] This is clearly not observed here. In any case we know that the Si-MCM-41 crystallites are stable under the recrystallisation conditions and that complete dissolution of the parent Si-MCM-41 does not occur.[6,7,11] (ii) Some silica (mainly amorphous phase) from the parent Si-MCM-41 can dissolve and interact with the Al to create a new separate Al-MCM-41 phase which coexists with the original preserved crystallites of the parent Si-MCM-41. However in such a scenario, the same amount of silica will dissolve (regardless of the recrystallisation gel Si/Al ratio) and therefore the resulting recrystallised samples should be substantially the same (irrespective of gel Si/Al ratio) with any excess Al existing as an alumina phase. This is, however, not likely since the nature of the recrystallised samples reported here is strongly dependent on the gel Si/Al ratio.

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