

Super-microporous aluminosilicate catalysts *via* primary amine templating

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Super-microporous aluminosilicate catalysts possessing pores in the range 14–20 Å may be prepared *via* primary amine templating alone or in combination with post-synthesis Al-grafting.

The design and synthesis of materials that have a well defined pore structure similar to that of zeolites, but with larger pores, has been a main research goal in solid acid catalysis over the past decade.¹ Recent advances, which include the synthesis of the M41S family of mesoporous solids,² have to some extent achieved this goal. Many other varieties of mesoporous materials with pores of size typically above 25 Å have been prepared.³ Until recently, much less attention has been paid to the synthesis of materials with pores in the super-microporous (10–20 Å) range. Solid acid materials in this pore size range are important since they bridge the gap between microporous zeolites and mesoporous materials. Bagshaw and Hayman⁴ used ω -hydroxy-bolaform surfactants to template the formation of super-microporous silicas. Zhao *et al.*⁵ reported the preparation of MCM-41 materials with tailored pore openings in the super-microporous range. Sun *et al.*⁶ used adamantanamine while Serrano *et al.*⁷ employed cetyltrimethylammonium or dodecyltrimethylammonium ions for the formation of microporous materials. Here we report the primary amine templated synthesis of super-microporous aluminosilicate materials whose pore size can be further tailored *via* post-synthesis grafting of Al. Post-synthesis grafting of extra Al also serves to remarkably improve the acidity and catalytic activity of the materials.

We have previously reported on the preparation of *mesoporous* aluminosilicates (Al-MMS, Al-HMS)^{8–10} using the primary amine templating route.¹¹ Our previous work has shown that the pore size of Al-MMS (Al-HMS) materials is to some extent dependent on the alkyl chain length of the primary amine template with longer amines resulting in larger pores.^{12,13} The pore size was also found to be dependent on the Si/Al ratio, *i.e.* the pore size was reduced at low Si/Al ratios.^{8–10,12,13} This meant that pore sizes at the lower end of the mesopore range (*ca.* 20 Å) were only obtainable for highly aluminous samples and that pores in the super-microporous range (10–20 Å) could not be achieved even at Si/Al ratios as low as 7.^{8–10,12,13} Previous work has also shown that materials prepared at gel Si/Al ratios in the range 80–1 always have higher than expected Si/Al ratios implying relatively low levels of Al incorporation into the solid products.^{8–10,12,13} We have now found that it is possible to circumvent the limitation on the lowest pore size obtainable by improving the incorporation of Al. This is achieved by modifying our previous synthesis procedure¹⁰ so as to ensure optimum dissolution of the Al source. Furthermore performing post-synthesis grafting of extra Al can reduce the pore size of the resulting materials further.

The synthesis procedure used¹⁰ was modified as follows: desired quantities of aluminium isopropoxide (Al(*i*-C₃H₇O)₃) were dispersed in 35 ml of isopropyl alcohol with vigorous mechanical stirring at 70 °C for 15 min in order to dissolve the highest possible amount of the aluminium source. The resulting

solution was cooled to room temperature and then added under magnetic stirring to a solution of 0.2 mol tetraethyl orthosilicate (TEOS) in 80 ml of absolute ethanol. The resulting mixture was then heated at 70 °C under vigorous stirring for 4 h to obtain the polymerised Si–O–Al species. After cooling to room temperature (under stirring) the inorganic precursor was added to a clear solution of 0.05 mol dodecylamine (DDA) in a mixture of 80 ml of deionised water and 120 ml of absolute ethanol under slow stirring. The stirring was maintained for 5 min after which the resulting mixture was allowed to age at room temperature for 20 h. The solid product was obtained by filtration, washed with two portions of 100 ml of ethanol, air-dried overnight at room temperature and finally calcined in air at 650 °C for 4 h. This procedure was used to prepare aluminosilicate materials with Si/Al molar ratios of 40:1, 20:1 and 10:1, designated Al-MMSX where X is the synthesis gel Si/Al ratio. Al-grafting was performed on the Al-MMSX samples as follows: 1.28 g of a solution of chlorhydrol ([Al₂Cl(OH)₅·2H₂O], 6.4 mol l⁻¹ with respect to aluminium) was dissolved in 50 ml of distilled water and stirred at 80 °C for 1 h. 1.0 g of Al-MMSX was added to the solution and the resulting suspension stirred for a further hour at 80 °C. After cooling to room temperature, the solid was filtered off and washed with distilled water until free of Cl⁻ ions, dried in the oven at 100 °C and finally calcined at 500 °C for 4 h. The resulting Al-grafted materials were designated AlAl-MMSX.

The elemental compositions, *d* spacing and textural properties of the present Al-MMS materials are shown in Table 1 and 2. The bulk Si/Al ratios of the samples indicate that Si and Al are incorporated into the solid framework in proportions closely related to the synthesis gel composition. A significant observation is that Al-MMS40 and Al-MMS10 are Al rich, *i.e.* a greater proportion of Al in the synthesis gel is incorporated into the solid product compared to Si. This is a departure from our previous studies where we always obtained silica rich materials.^{8–10,12,13} The modified synthesis procedure used here, in which the dissolution of the Al source is optimised, therefore allows for greater Al incorporation into the solid product. The *d* spacings of the present Al-MMS samples (see Table 2) are in all cases lower (by *ca.* 5%) than those we have previously

Table 1 Elemental composition, acid content and catalytic activity of super-microporous Al-MMS samples

Sample	Si/Al	Acid content/ mmol g ⁻¹	Cumene conversion (%) ^a	
			50 min	150 min
Al-MMS40	39.0	0.36	35	28
AlAl-MMS40	22.8	0.57	53	47
Al-MMS20	22.0	0.56	47	41
AlAl-MMS20	14.9	0.75	59	54
Al-MMS10	9.0	0.73	59	51
AlAl-MMS10	7.4	0.82	67	60

^a The conversion of cumene was performed in a tubular stainless steel, continuous flow, fixed-bed microreactor system with helium as carrier gas at 300 °C as previously described in ref. 10.

Table 2 Textural properties of super-microporous Al-MMS samples; values in parenthesis are micropore surface area and volume

Sample	Basal (d_{100}) spacing/Å	Surface area/ $\text{m}^2 \text{g}^{-1}$	Pore volume/ $\text{cm}^3 \text{g}^{-1}$	Pore size/Å
Al-MMS40	32.4	1023 (488)	0.45 (0.18)	20.5
AlAl-MMS40	32.0	643 (406)	0.33 (0.17)	17.7
Al-MMS20	31.1	864 (497)	0.38 (0.19)	18.4
AlAl-MMS20	30.2	562 (403)	0.28 (0.17)	16.3
Al-MMS10	30.5	684 (520)	0.31 (0.20)	17.7
AlAl-MMS10	29.8	358 (286)	0.24 (0.18)	14.5

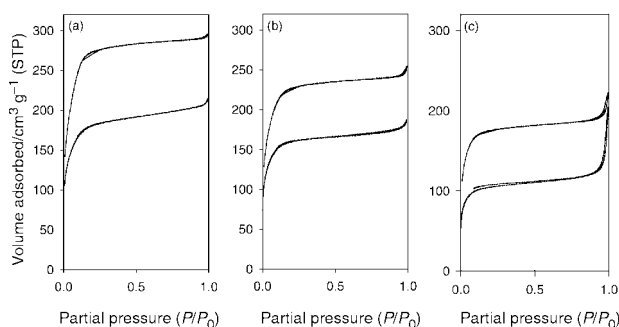


Fig. 1 Nitrogen sorption isotherms of super-microporous primary amine templated aluminosilicates, prepared at gel Si/Al ratios of (a) 40, (b) 20, (c) 10, before (top) and after (bottom) post-synthesis grafting of Al.

observed.¹⁰ It is worth noting that the d spacings observed here are generally lower than those normally obtained for M41S type mesoporous materials.^{1–3} Powder XRD patterns (not shown), for the present Al-MMS samples are similar to those of comparable mesoporous materials,^{10–14} *i.e.* comprising of a single (100) peak at low 2θ values. This is an indication that the present samples are as well ordered as any other primary amine templated mesoporous aluminosilicates.

The clearest indication that the greater Al incorporation attained here results in materials with super-microporous rather than mesoporous character is given by the textural parameters in Table 2. The surface area, pore volume and pore size obtained for the present samples are generally lower than those previously observed for mesoporous Al-MMS (Al-HMS) materials.^{10–14} We have previously reported surface areas of 1200, 1195 and 967 $\text{m}^2 \text{g}^{-1}$, and pore volumes of 0.65, 0.52 and 0.49 $\text{cm}^3 \text{g}^{-1}$ for mesoporous Al-MMS materials prepared (with dodecylamine as template) at gel Si/Al ratios of 40, 20 and 10, respectively.¹⁰ The pore volumes of the present samples are therefore at least 30% lower than those of analogous mesoporous materials.¹⁰ A particular feature of the present Al-MMS samples is that they exhibit a high proportion of micropore surface area and volume as shown in Table 2. The pore size of the materials (obtained using BJH analysis) is, as shown in Table 2, clearly in the super-microporous range. This is illustrated by the N_2 sorption isotherms shown in Fig. 1. The isotherms exhibit high adsorption at low ($P/P_0 < 0.2$) partial pressures which is characteristic of super-microporous materials. The isotherms do not exhibit the mesopore filling step (at $P/P_0 > 0.2$) normally observed for mesoporous materials.

We have found that performing post-synthesis grafting of Al can increase the microporous character of the Al-MMS samples. The effect of Al-grafting on pore size and porosity is illustrated in Fig. 1; the super-micropore filling step is shifted to lower partial pressures (lower pore size) after grafting. As shown in Table 2, the pore size of AlAl-MMS samples is lower than that of Al-MMS materials by 2–3 Å. This reduction in pore size is accompanied by a decrease in surface area and pore volume, which in turn leads to an increase in the *proportion* of micropore surface area and volume. Indeed sample AlAl-MMS10 is virtually microporous, with a pore size of 14.5 Å and the proportion of micropore surface area and volume is above

75%. It is likely that the Al is grafted into the pore walls thus reducing the pore size. This does not, however, effect the basal spacing (see Table 2). We note that structural ordering (as indicated by powder XRD) is largely unaffected by the grafting process. In addition to tailoring the pore size, Al-grafting also increases the acid content and catalytic activity as shown in Table 1. (The acid content was determined by exposing the samples to cyclohexylamine for 16 h following which they were heated at 100 °C for 4 h to remove physisorbed amine. The samples were then subjected to thermogravimetric analysis and the weight loss between 240 and 420 °C was used to calculate the acid content assuming that each acid site interacts with one base molecule.⁹) The increase in acid content is greatest for AlAl-MMS40 (*ca.* 60%) and lowest for AlAl-MMS10 (*ca.* 12%). The increase in acidity is reflected by the higher cumene cracking¹⁰ activity for the AlAl-MMS samples. Interestingly, the sample (Al-MMS10) with the highest cation exchange capacity (CEC = 42 meq./100 g) takes up less ‘extra Al’ than Al-MMS40 with a CEC of 12 meq./100 g. (CECs were measured using the Kjeldahl method after NH_4^+ exchange.) This implies that the take up of extra Al is not entirely an ion exchange process. Rather it appears that grafting also occurs on silanol groups as previously described.^{15,16} The take up of extra Al is therefore consistent with our previous observation that the concentration of silanols in Al-MMS type materials decreases with Al content.¹⁰ Indeed under similar grafting conditions the pure silica material incorporates at least twice as much Al as the Al-MMS samples.

Primary amine templating of mesostructured aluminosilicates is known to provide solid acid catalysts whose activity is generally higher than that of materials prepared *via* quaternary ammonium ion templating.^{10,12,17} Recently, it has also been shown that the wormhole-like structure of primary amine templated aluminosilicates has three-dimensional connectivity.¹⁸ Such connectivity is an important factor with respect to catalytic activity. This report therefore represents the first synthesis of super-microporous aluminosilicates with three-dimensional connectivity. These super-microporous materials combine all the advantages of primary amine templated aluminosilicates, and also offer the potential for size and shape selective catalysis of large substrates, which is not possible for mesoporous materials.

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Notes and references

- 1 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
- 2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 3 J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.
- 4 S. A. Bagshaw and A. R. Hayman, *Chem. Commun.*, 2000, 533.
- 5 X. S. Zhao, G. Q. Lu and X. Hu, *Chem. Commun.*, 1999, 1391.
- 6 T. Sun, M. S. Wong and J. Y. Ying, *Chem. Commun.*, 2000, 2057.
- 7 D. P. Serrano, J. Aguado, J. M. Escola and E. Garagorri, *Chem. Commun.*, 2000, 2041.
- 8 R. Mokaya and W. Jones, *Chem. Commun.*, 1996, 981.
- 9 R. Mokaya and W. Jones, *Chem. Commun.*, 1996, 983.
- 10 R. Mokaya and W. Jones, *J. Catal.*, 1997, **172**, 211.
- 11 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
- 12 R. Mokaya and W. Jones, *Catal. Lett.*, 1997, **49**, 87.
- 13 R. Mokaya and W. Jones, *J. Mater. Chem.*, 1998, **8**, 2819.
- 14 W. Z. Zhang, T. R. Pauly and T. J. Pinnavaia, *Chem. Mater.*, 1997, **9**, 2491.
- 15 R. Mokaya and W. Jones, *Phys. Chem. Chem. Phys.*, 1999, **1**, 207.
- 16 R. Mokaya and W. Jones, *J. Mater. Chem.*, 1999, **9**, 555.
- 17 T. J. Pinnavaia and W. Z. Zhang, *Stud. Surf. Sci. Catal.*, 1998, **117**, 23.
- 18 J. Lee, S. Yoon, S. M. Oh, C. H. Shin and T. Hyeon, *Adv. Mater.*, 2000, **12**, 359.