

Post-synthesis grafting of Al onto MCM-41

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Al-containing MCM-41 materials are prepared by grafting Al onto purely siliceous MCM-41; the resulting materials retain the hexagonal order and physical properties of the purely siliceous parent MCM-41 and exhibit higher Brønsted acid content compared to Al-MCM-41 prepared by direct hydrothermal synthesis.

The recent synthesis of the M41S family of siliceous solids with sharply distributed pores of diameter in the mesoporous regime (20–100 Å) has greatly increased the range of heterogeneous catalysts.^{1–3} Of particular interest is MCM-41 which possesses a hexagonally arranged array of uniform pores. Brønsted acid sites may be generated in MCM-41 by isomorphous substitution of Al for Si.^{2,3} However, the direct synthesis of aluminium containing MCM-41 has proved to be challenging; the incorporation of even small amounts of aluminium in the MCM-41 framework causes a decrease in hexagonal ordering.^{4,5} It has also been observed that when compared to zeolites, the concentration of Brønsted acid sites in such aluminosilicate MCM-41 is very low even at high aluminium concentrations.^{2,3,6} It is therefore desirable to prepare aluminosilicate MCM-41 which exhibits both higher Brønsted acid content and long range order similar to that of the purely siliceous material. An alternative synthetic approach which may address both these challenges is the post synthesis grafting/incorporation of aluminium into MCM-41. This is possible due to the presence of a high density of silanol groups on the pore surface of MCM-41 to which guest species may be attached.^{7–9} Here we report a grafting method which consists of reacting the silanol groups present in MCM-41 with discrete amounts of aluminium alkoxide in a non-aqueous environment, followed by calcination to anchor the Al.

The starting material, a purely siliceous MCM-41 (designated PSMCM), was prepared by adding tetramethylammonium hydroxide (TMAOH) and sodium hydroxide (NaOH) to an aqueous solution of hexadecyltrimethylammonium chloride (CTACl) of appropriate concentration with stirring for 10 min. Tetraethylorthosilicate (TEOS) was combined with the resulting solution at room temp. under stirring to give a gel of molar composition 0.25 TEOS:0.06 NaOH:0.03 TMAOH:27.8 H₂O:0.06 CTACl which was left to react for 24 h at room temp. The solid product was obtained by filtration, washed with distilled water, dried in air at room temp. and finally calcined at 550 °C for 16 h. For alumination, 2.0 g of PSMCM was dispersed in 50 ml dry hexane, and added to 150 ml dry hexane containing the appropriate amount of aluminium isopropoxide,

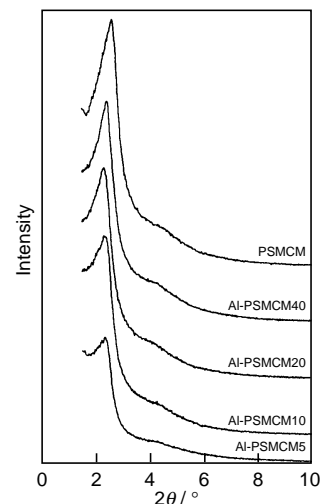


Fig. 1 Powder XRD patterns of calcined purely siliceous sample (PSMCM) and Al-grafted (Al-PSMCM) samples

Al(OPr)ⁱ₃, to give Si:Al ratio in the range 40–5:1. The resulting mixture was stirred for 10 min and allowed to react at room temp. for 24 h. The obtained powder was filtered, washed with dry hexane, dried at room temp. and calcined at 550 °C for 4 h. Four samples (designated Al-PSMCMX, where X is the Si:Al ratio) were prepared from PSMCM at Si/Al ratio 40, 20, 10 and 5.

Fig. 1 shows that the powder X-ray diffraction patterns of the Al grafted materials are similar to that of the parent MCM-41 which is an indication that hexagonal order is maintained. TEM shows that, despite the gradual reduction in the intensity of the (100) peak, the hexagonal arrangement of the pores remains the same in all cases. Chemical analysis given in Table 1 shows that the Si/Al molar ratios of the Al-grafted samples are close to the expected bulk Si/Al ratios which is an indication of the potential of the present method in introducing discrete amounts of heteroatoms to purely siliceous MCM-41. ²⁷Al MAS NMR spectra (of the calcined samples) shown in Fig. 2 indicate that all the samples contain tetrahedral (framework) and octahedral (non-framework) Al with resonances at δ 53.0 and 0, respectively. The amount of tetrahedral Al is always higher than the octahedral Al and generally increases with increasing Al content. For the dry samples, octahedral Al was always higher

Table 1 Elemental composition, *d* spacing and textural properties and acidity of the study materials (CHA = cyclohexylamine)

Sample	Si/Al	<i>d</i> ₁₀₀ /Å	Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	APD ^a /Å	<i>a</i> ₀ ^b /Å	Wall thickness/Å	Acidity/mmol CHA g ⁻¹
PSMCM		33.8	1110	0.93	26.3	39.0	12.7	
Al-PSMCM40	38.5	34.8	1000	0.82	26.8	40.2	13.4	0.16
Al-PSMCM20	19.8	36.4	1004	0.81	26.7	42.0	15.3	0.29
Al-PSMCM10	11.2	36.0	996	0.78	26.6	41.6	14.9	0.48
Al-PSMCM5	6.1	35.7	980	0.77	26.5	41.2	14.7	0.51

^a APD = Average pore diameter (determined using BJH analysis). ^b *a*₀ = Lattice parameter from XRD data using the formula *a*₀ = 2*d*₁₀₀/√3.

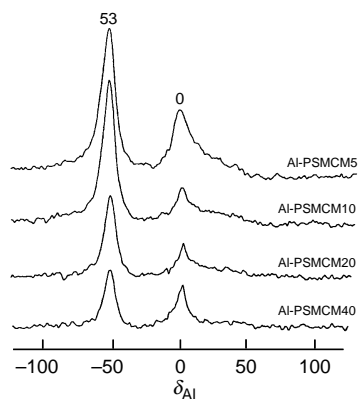


Fig. 2 ^{27}Al MAS NMR spectra of calcined Al-PSMCM samples. To ensure quantitative reliability all samples were hydrated and equilibrated with room air prior to measurement.

than tetrahedral Al and therefore calcination serves to anchor some (octahedral) Al to the framework.

The d spacing of the Al-grafted materials was in all cases higher than that of the parent MCM-41 (see Table 1). This is consistent with the presence of tetrahedral Al in the framework. Table 1 also gives the textural properties obtained for the calcined Al-PSMCM materials. The surface area and average pore diameter (obtained by BJH analysis of the sorption data) of the Al-PSMCM materials are similar to that of the parent MCM-41 while the pore volume is lower probably due to the presence of non-framework Al in the pores. The pore wall thickness of the Al-grafted samples was in all cases higher than that of the parent purely siliceous MCM-41 sample in agreement with the incorporation of Al into the framework.

The acid content of the Al-PSMCM materials was obtained using thermally programmed desorption of cyclohexylamine.³ Prior to analysis the base containing samples were heat treated at 250 °C for 2 h. This method principally determines the proton concentration which is of interest to catalysis. It is clear from the acidity values in Table 1 that the Al-grafting process generates acid sites and that the number of acid sites generated increases as the amount of framework aluminium increases. The acid content of Al-PSMCM10 and Al-PSMCM5 are very close in agreement with the ^{27}Al MAS NMR which shows them to possess almost similar amounts of tetrahedral Al. We found that for similar bulk Si/Al ratios, the acidity of Al-PSMCM samples is higher than that of equivalent (protonic) aluminosilicate MCM-41 prepared using the conventional direct synthesis method (for example $\text{H}^+\text{-MCM-41-20}$ (see ref. 3 for sample details) had an acid content of 0.19 mmol g^{-1} compared to 0.29 mmol g^{-1} for Al-PSMCM20. We also prepared Al-grafted amorphous silica (designated SA10) at a Si/Al ratio of 10; the resulting material had an acid content of 0.22 mmol g^{-1} compared to 0.48 for the equivalent (in terms of Al content) Al-PSMCM10 sample. Confirmation of the higher acid content of Al-grafted samples was provided by their activity in the cracking of cumene as shown in Fig. 3. The reaction, performed at 300 °C and a WHSV of 5.5 using a tubular stainless steel, continuous flow fixed-bed microreactor system with helium (25 ml min^{-1}) as carrier gas after activating the catalyst bed (100 mg; 30–60 mesh) for 1.5 h at 500 °C under helium (25 ml min^{-1}) proceeded almost exclusively *via* catalytic cracking to benzene and propene with only trace amounts of α -methylstyrene (product of dehydrogenation over Lewis acid sites) indicating that the active sites are of the Brønsted type.¹⁰ The curves in Fig. 3 indicate that Al-PSMCM materials possess considerable catalytic activity, with the conversion of cumene increasing with increasing acid content and amount of frame-

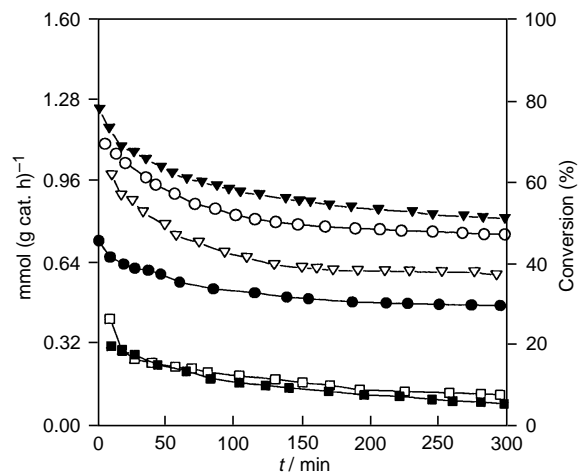


Fig. 3 Cumene conversion over Al-PSMCM samples and reference materials compared at 300 °C and WHSV of 5.5. Al-PSMCM5 (\blacktriangledown), Al-PSMCM10 (\circ), Al-PSMCM20 (∇), Al-PSMCM40 (\bullet), $\text{H}^+\text{-MCM-41-20}$ (\square), and SA10 (\blacksquare)

work aluminium. In particular we note that the activity of the Al-PSMCM materials is superior to that of equivalent MCM-41 prepared by direct synthesis (see comparison between $\text{H}^+\text{-MCM-41-20}$ and Al-PSMCM20). The Al-grafted amorphous silica (SA10), in line with the acid content, had a much lower activity compared to the equivalent Al-grafted MCM-41 (Al-PSMCM10). The purely siliceous material exhibited no catalytic activity.

We have demonstrated that Al-containing MCM-41 of good order can be prepared by post-synthesis grafting of Al by reacting purely siliceous MCM-41 with an Al-alkoxide in non-aqueous media. The Al is incorporated into the framework to generate materials with Brønsted acid sites whose content is higher than in equivalent Al-MCM-41 materials prepared *via* the conventional direct synthesis method. We attribute the higher acid content in the Al-grafted materials to the presence of Brønsted acid generating Al in accessible sites on the pore walls.

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Footnote and References

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- 1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 2 A. Corma, V. Fornés, M. T. Navarro and J. Pérez-Pariente, *J. Catal.*, 1994, **148**, 569.
- 3 R. Mokaya, W. Jones, Z. Luan, M. D. Alba and J. Klinowski, *Catal. Lett.*, 1996, **37**, 113.
- 4 C. Y. Chen, S. L. Burkett, H-X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 27.
- 5 Z. H. Luan, H. Y. He, W. Z. Zhou, C. F. Cheng and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2955.
- 6 J. Weglarski, J. Datka, H. Y. He and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 5161.
- 7 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.
- 8 R. Anwender and R. Roesky, *J. Chem. Soc., Dalton Trans.*, 1997, 137.
- 9 H. Hamdan, S. Endud, H-Y. He, M. N. M. Muhid and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2311.
- 10 J. W. Ward, *J. Catal.*, 1967, **9**, 225; 1968, **11**, 251, 259.

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