Synthesis, Characterization, and Catalytic Activity of Beidellite–Montmorillonite Layered Silicates and their Pillared Analogues

Paul A. Diddams,[a] John M. Thomas,*[a] William Jones,[a] James A. Ballantine,[b] and J. Howard Purnell[b]

[a] *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*
[b] *Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, U.K.*

A synthetic beidellite-smectite, characterized by a range of techniques, including high-resolution ^{27}Al and ^{29}Si solid-state n.m.r. spectroscopy, shows interesting catalytic activity (in secondary amine formation from cyclohexylamine, in ester production from hex-1-ene and acetic acid, and in ether synthesis from pentanol): the selectivities differ significantly from those of montmorillonite-smectites.

Apart from their intrinsic lack of good crystalline order, naturally-occurring sheet silicates which, in their cation-exchanged and/or pillared forms, function as efficient catalysts[1] for a wide range of organic reactions, also tend to contain a variety of paramagnetic impurities. Such impurities can frustrate attempts at fuller characterization of the components that make up the individual aluminosilicate sheets or the pillars that can be introduced to improve the high-temperature stability of these catalysts. Thus n.m.r. spectroscopy, which is also invaluable for monitoring the course of interlamellar catalysed reactions,[2] can be employed only with a few 'high-purity' natural clays, or with commercially available synthetic fluorohectorites that are not well crystallized. There would be considerable advantages in utilizing relatively well-ordered synthesized sheet silicates: these could then be extensively characterized and their catalytic performance assessed.

We report here the synthesis of an expandable beidellite [idealized formula $M_x^+(Si_{8-x}Al_x)^{tet.}(Al_4)^{oct.}O_{20}(OH)_4$] of high cation-exchange capacity and upon its catalytic selectivities for three proton-catalysed organic reactions. The results emphasize the catalytic potential of exploiting the consequences of the shift of the surplus negative charge from the octahedral component of the smectite sheet, as in montmorillonite [idealized formula $M_y^+ (Si_8)^{tet.}(Al_{4-y}Mg_y)^{oct.}O_{20}(OH)_4$], to the tetrahedral one. (Note, $0.5 \leq x \approx y \leq 1.2$.)

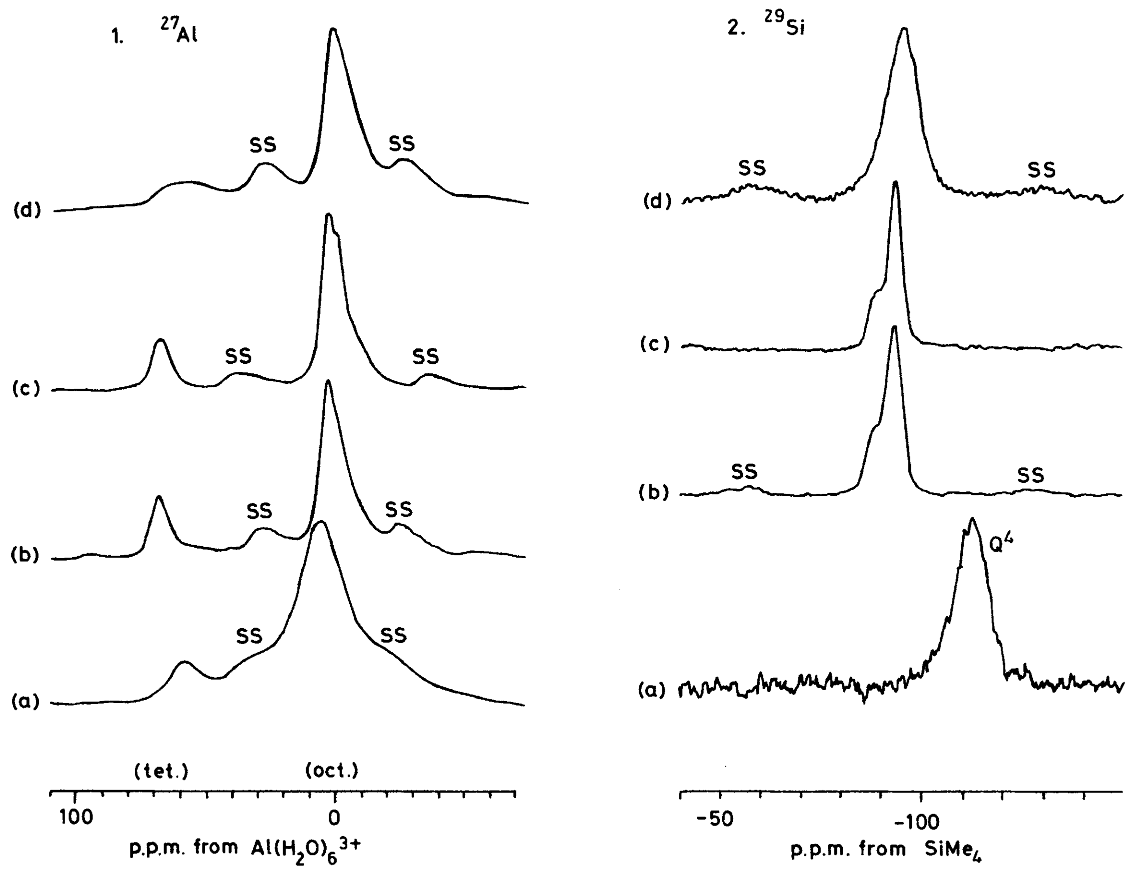


Figure 1. ^{27}Al and ^{29}Si Magic-angle spinning n.m.r. spectra of (a) dried gel precursor used for synthesis; (b) Na^+-exchanged synthetic beidellite; (c) Al^{3+}-exchanged variant of (b); (d) Al-pillared variant (see text) of (b). Spectra referred to free $Al(H_2O)_6^{3+}$ (for ^{27}Al) and to tetramethylsilane (^{29}Si). Peaks labelled SS are spinning side-bands. The precursor gel is seen to contain its silicon predominantly in $Si(OSi)_4$ environments (Q^4), but some $Si(OSi)_3(OAl)$ cannot be ruled out, ref. 12.

The synthesis was performed[3] hydrothermally using an aqueous gel containing SiO_2, Al_2O_3, and MgO in the molar ratios 16:3.5:1. *X*-Ray diffraction (at various stages in the synthesis), ^{29}Si and ^{27}Al magic-angle spinning (m.a.s.) n.m.r and i.r. spectroscopy, thermogravimetric and chemical analysis, and analytical electron microscopy showed that a di-octahedral smectite was formed with only Al present in the octahedral sheet and the Mg present as exchangeable cations. The fact that the smectite could still be expanded (from *ca.* 10.0 to 17.2 Å on treatment with ethylene glycol) after the Li^+-exchanged form was heated at 250 °C for 12 h, confirmed[4] the identification of the smectite as beidellite. Its cation exchange capacity was 109 ± 8 mequiv. per 100 g of dehydrated form, corresponding to layer charge per formula unit of 0.78 ± 0.06. It could be pillared by treating its Na^+-exchanged form with the multinuclear cation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, generated from chlorhydrol by standard methods,[5] and calcined at 500 °C. The interlamellar distance in the pillared beidellite after calcination was *ca.* 18 Å, compared with 10.0 Å for the original synthetic material after dehydration at 150 °C. Its surface area (determined by the N_2 Brunauer–Emmett–Teller method) was 153 ± 5 m^2g^{-1}.

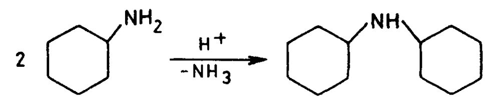
The solid state n.m.r. studies[6] were particularly revealing (Figure 1). Some tetrahedrally as well as octahedrally co-ordinated Al, readily distinguished in ^{27}Al n.m.r. studies,[6,7] exists in the gel precursor, and the presence of the tetrahedrally co-ordinated Al in the synthesized beidellite is beyond dispute [see peaks at *ca.* 70 p.p.m. with respect to $Al(H_2O)_6{}^{3+}$, Figure 1.1(b) and (c)]. The pronounced extra shoulder in the octahedral Al signal obtained from the Al^{3+}-exchanged beidellite [Figure 1.1 (c)] is attributed to the mobile interlamellar cations, an assignment confirmed by n.m.r. experiments on static samples. There appear to be at least two types of tetrahedrally bonded Al sites in the pillared form [see region from 55 to 75 p.p.m. in Figure 1.1 (d)]. In view of well-known[8] problems associated with obtaining quantitatively reliable ratios of $(Al)^{tet.}/(Al)^{oct.}$ from ^{27}Al m.a.s./n.m.r. spectra, no attempt was made to establish empirical formulae by this method.

The ^{29}Si m.a.s./n.m.r. spectra (Figure 1.2) were, in contrast, of considerable value in estimating the Si/Al ratios in the tetrahedral manifold of the beidellite. A variant[9,2c] of the equation,[10] based on Leowenstein's rule, which states that no Al–O–Al links exist in a tetrahedral structure for an aluminosilicate is shown in equation (1), where I = n.m.r. peak

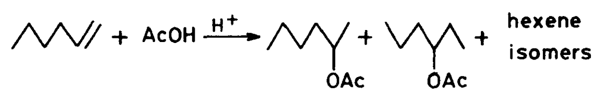
$$(Si/Al)^{tet.} = \sum_{n=0}^{n=3} I_{Si(nAl)} \Big/ \sum_{n=0}^{n=3} \tfrac{n}{3}\, I_{Si(nAl)} \qquad (1)$$

intensity. Using equation (1) we estimated, from the deconvoluted (gaussian) peaks in Figures 1.2(b) and (c), that the $(Si/Al)^{tet.}$ ratio is 11.5 ± 1.0. [The assignment of the ^{29}Si peaks at −88 and −93 p.p.m. to $-Si(OSi)_2(OAl)$ and $-Si(OSi)_3$ respectively is in agreement with the independent conclusions of Serratosa *et al.*[9] who have examined the ^{29}Si spectra of a range of micas.] We conclude from the ^{29}Si m.a.s. n.m.r. spectra that the composition of the tetrahedral manifold is $Si_{7.35(\pm 0.08)}Al_{0.65(\pm 0.08)}$ a range which is compatible with the value of the layer charge (0.78 ± 0.06) determined by chemical methods.

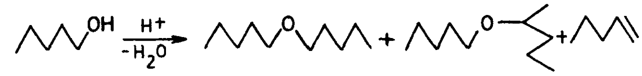
The catalytic activity of the Al^{3+}-exchanged, as-synthesized and pillared beidellite was compared with that of a standard, naturally occurring montmorillonite clay [known as Gelwhite, see refs. 1(c) and 2(a) for full characterization] treated in an identical fashion. The synthesis of secondary amines [typified by conversion of cyclohexylamine (1) into the secondary



(1) **(2)**



(3) **(4a)** **(4b)**



(5) **(6a)** **(6b)** **(7)**

Table 1. Catalytic performance of synthetic beidellite (B) and of naturally occurring montmorillonite (M) and their pillared analogues (all Al^{3+}-exchanged). Total yields expressed as mol %.

	B	M	Pillared-B	Pillared-M
Amine formation (1) → (2)	24.9	27.9	6.5	1.7
Hex-1-ene (3) + AcOH	12.0	34.1	2.2	0.3
Percentage of:				
hex-2-yl acetate (**4a**)	50.6	23.2	66.2	100
hex-3-yl acetate (**4b**)	14.2	10.2	9.4	—
hexene isomers	35.2	66.6	24.4	—
Ether formation from n-pentanol (**5**)	42.0	54.5	6.3	1.9
Percentage of:				
1,1-dipentyl ether (**6a**)	56.8	46.5	60.5	63.9
1,2-dipentyl ether (**6b**)	4.8	5.1	3.8	28.0
pent-1-ene (7)	38.4	48.4	35.7	8.1

amine (**2**)], the formation of esters (**4a**) and (**4b**) and hexene isomers from (**3**) and acetic acid, and the synthesis of ethers (**6a**) and (**6b**) from pentanol (all proton-catalysed), were the reactions selected. All were carried out under conditions described elsewhere (160 to 210 °C for 4 h).[1,11] The yields were as shown in Table 1, from which we conclude that Al^{3+}-exchanged beidellite and the corresponding montmorillonite (i) are of comparable activity for secondary amine formation; (ii) differ by a factor of three in overall yield for the ester formation, the selectivity for the hex-2-yl product being twice as large, and for the hexene isomers half as much, in the case of the synthetic beidellite as for the natural clay; (iii) differ slightly so far as overall yield of ethers is concerned, there being a small but significant enhancement of selectivity for the 1,1-dipentyl ether for the beidellite; (iv) total yields for the pillared clays are much less than for the unpillared precursors; but the drop is smaller, and the selectivities significantly different, for the beidellite than for the natural clay.

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