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Organometallic cation-exchanged phyllosilicates: A high spacing intercalate formed from *N*-methyl-(3-triphenylstannyl)pyridinium exchanged montmorillonite

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N-methyl-3-(triphenylstannyl)pyridinium cations have been prepared and exchanged with sodium ions of montmorillonite to yield a pillar-interlayered phyllosilicate with d(001) = 19.1 Å (hydrated) or 17.7 Å after pumping in vacuo. ^{119}Sn Mössbauer spectroscopy is used to characterise the structure and interlayer environment of the cation.

Keywords: Organotin, montmorillonite, phyllosilicate Mössbauer, cation-exchange

INTRODUCTION

In the search for stable, high surface area modifications of smectites for utilisation as catalysts or selective sorbents, considerable attention has focused on the cationic derivatives of carbon and silicon as interlayer counterions. In particular, organic derivatives of the ammonium ion[1] and silicon in the form of silica[2–4] have been the basis of several detailed studies. In contrast, the lower members of main group IV have received scant attention, possibly because their chemistry generates neutral or anionic complexes more readily than cationic ones. Despite such limitations, a study of tin exchanged clays has suggested itself as being both rich and varied, a suggestion fostered by three complementary considerations. Firstly, tin has an extensive chemistry, embracing two stable oxidation states, coordination numbers of two through eight and a rationalisable synthetic organometallic chemistry. This provides a number of opportunities to tailor the molecular architecture of the cation which can be used to fabricate materials with high interlayer surface areas and large pore volumes, similar to layer silicates exchanged with bulky, highly charged cations such as $[Al_{13}O_4(OH)_{24}(H_2O)_{42}]^{7+}$,[5] $Fe(C_{10}H_8N_2)_3{}^{3+}$,[6,7] and, more recently, metal complex catalysts such as $RhH(CO)_x(PPh_3)_2$ ($x = 1, 2$) which can be immobilised by intercalation in clay minerals such as montmorillonite.[8–10] Secondly, Mössbauer spectroscopy provides a direct, in situ probe of the tin-bearing species, yielding data from which oxidation state, local geometry and tightness of binding of the tin atom within the host can be deduced. Finally, the increasing commercial utilisation of organotin compounds, as, for example, agrochemicals, has given rise to justifiable concern over their environmental degradation pathway. Our work may help clarify the nature and residence time of these species in clay bearing soils.

The goal of our work on cation-exchanged clay materials is the preparation of catalytically active systems, in which the efficiency of the catalyst toward a particular reaction is maximised by synthetic control of the interlayer spacing within the clay and the nature of its associated cation. Montmorillonite clays are known to catalyse a wide variety of important organic reactions, including the formation of di-alkylethers via high temperature (> 100°C) dehydration of alcohols[11] or low temperature (< 70°C) conversion of alk-1-enes,[12] the hydration of ethene,[13] the esterification of organic acids by alkenes,[14] the low temperature synthesis of methyltertiarybutylether (MTBE) from 2-methylpropene and methanol,[15] and the reaction of alcohols to form *t*-butylethers.[16] Applications toward cracking processes are also known.[17]

In this paper, we describe the preparation and

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characterisation of a montmorillonite clay with an organotin cation as the interlayer gegenion. This work exemplifies our current philosophy towards the preparation of high-spacing phyllosilicate materials, and is a specific example of what should be a general and extremely adaptable methodology. The criteria we require in the cation is that it is of spherical symmetry (to negate undesirable orientations between silicate layers) and is bonded to rigid (conformationally inflexible) ligands, so that the molecular dimensions of the cation prior to exchange can be used to predict, and hence dictate, the interlayer spacing. The choice of the 3-(triphenylstannyl)pyridinium cation is a simple monovalent manifestation of these criteria, and, in addition, incorporates a Mössbauer active nucleus (^{119}Sn) to aid the characterisation of the cation exchanged clay.

EXPERIMENTAL

3-bromopyridine (Aldrich) and anhydrous $SnCl_4$ (Alfa) were of commercial origin and were used without further purification. Solvents were dried before use by conventional methods. The Wyoming montmorillonite used was the $<2\,\mu m$ fraction of a sample supplied by Volclay Ltd, Wallasey, Cheshire. Chemical analysis by standard literature methods[18] of the Na^+-exchanged montmorillonite produced results consistent with a layer formulation of $(Si_{3.9}Al_{0.1})$—$(Al_{1.33}Fe_{0.88}Mg_{0.59})O_{10}(OH)_2$. The cation exchange capacity of the Na^+-exchanged form, determined by a flame photometric method[19] was 68 ± 2 milliequivalents per 100 g of clay (meq/100 g clay).

Infrared and ^{1}H n.m.r. spectra were recorded on Perkin Elmer 599B and R12B spectrometers respectively. Details of our Mössbauer spectrometer, cryostat and temperature controller and related experimental procedures are given elsewhere.[20] C, H, N analyses were carried out by the Microanalytical Service, University College Dublin.

Synthesis of 3-(triphenylstannyl)pyridine (I)

n-BuLi (30 mmol) in hexane (20 cm^3) was added to a solution of 3-bromopyridine (4.74 g, 30 mmol) maintained at −45°C. To the resulting pale yellow solution was added an ether solution of triphenyltin chloride (11.56 g, 30 mmol), whereupon a white precipitate developed which took on a greyish tinge on warming to room temperature. Saturated ammonium chloride solution (100 cm^3) was added, and the insoluble material filtered. Recrystallisation of this solid from boiling toluene yielded the desired product (4.08 g, 32%), while only ca. 0.5 g of unidentified yellow solid was recovered from the ether extracts. 3-(Triphenylstannyl)pyridine: Analysis, C 64.55; H 4.10; N 3.16%. Calc. for $C_{23}H_{19}NSn$, C 64.52; H 4.48; N 3.27%. m.p. 216–217°C (lit. 220°C).[21] Mössbauer; IS = 1.25 mm s^{-1}; QS = 0.00 mm s^{-1}; full width at half height, $\Gamma = 1.14$ mm s^{-1}.

Synthesis of *N*-Methyl-3-(triphenylstannyl)pyridinium iodide (II)

3-(Triphenylstannyl)pyridine (4.0 g) was refluxed in methyl iodide (10 cm^3) for 15 min. Ethanol (20 cm^3) was added to the solution and the mixture filtered while still hot. The solution was concentrated to dryness in vacuo, washed with cold diethyl ether (50 cm^3) and the solid recrystallised from ether/ethanol (2:1) to yield the pyridinium salt as orange crystals (3.37 g, 63%) which turned yellow on heating above 100°C. *N*-Methyl-3-(triphenylstannyl)pyridinium iodide: Analysis, C 50.38; H 3.78; N 2.39; I 22.46%. Calc. for $C_{24}H_{22}INSn$, C 50.56; H 3.90; N 2.46; I 22.26%. m.p. 173–174°C (lit. 183–184°C).[21] ^{1}H n.m.r. 9.50 m, 8.60–8.00 m ($5H, C_5H_4N$); 7.80–7.40 m (15H, $(C_6H_5)_3Sn$); 4.55 s (NCH_3). Mössbauer, IS = 1.26 mm s^{-1}; QS = 0.51 mm s^{-1}; $\Gamma = 0.83$, 0.84 mm s^{-1}.

Preparation of *N*-methyl-3-(triphenylstannyl)pyridinium exchanged montmorillonite (III)

1 g of air dried Na^+-montmorillonite was added slowly with stirring to 40 cm^3 of methanol containing sufficient of (**II**) to just satisfy the cation exchange capacity of the clay used. The pH of the methanolic solution of (**II**) was 8.5 and remained unchanged after the addition of the clay. The suspension was allowed to stand, with occasional stirring, for 6 hours, after which the top 30 cm^3 of methanol was decanted off and the remaining slurry was washed three times with reagent grade methanol. The majority of the exchanged sample (**III**), was dried in air and stored for further use, except for a small portion of the slurry which was smeared on to a glass slide and allowed to dry in air. This produced an

oriented film for X-ray diffraction analyses, which were carried out using a Jeol JDS 8X diffractometer using Cu-Kα radiation at 40 kV and 30 mA. X-ray diffraction traces were recorded for the air dried sample as prepared above and on the same sample after it had been dehydrated by pumping at a vacuum of 10^{-2} mm Hg at 20°C for 16 hours. Thermogravimetric analyses were recorded on a Stanton Redcroft TG750 instrument at 20°C min^{-1} under a flow of dry nitrogen carrier gas at 50 cm^3 min^{-1}.

Analysis for tin incorporated into clay was carried out on a solution prepared by fusing 0.17 g cation-exchanged clay with molten NaOH, then extracting the fused mass with hydrochloric acid and diluting to 150 cm^3.[18] The solution was analysed for tin using an IL 357 atomic absorption spectrophotometer using a nitrous oxide flame and a detection wavelength of 235.5 nm. Analysis, wt. % Sn = 3.1. Calc. = 7.8. X-ray d(001), air dry (**III**) = 19.1 Å, dehydrated sample = 17.7 Å; Mössbauer, IS = 1.29; QS = 0.85 mm s^{-1}; Γ = 0.84, 0.99 mm s^{-1}.

RESULTS AND DISCUSSION

3-(Triphenylstannyl)pyridine has been prepared from the reaction of 3-lithiopyridine and triphenyltin chloride and subsequently converted to the *N*-methylpyridinium salt (Eqns. 1–3), following reactions previously described by Gilman and Goreau.[21]

$$3\text{-BrC}_5\text{H}_4\text{N} + n\text{-C}_4\text{H}_9\text{Li} \rightarrow 3\text{-LiC}_5\text{H}_4\text{N} + n\text{-C}_4\text{H}_9\text{Br} \quad [1]$$

$$3\text{-LiC}_5\text{H}_4\text{N} + (\text{C}_6\text{H}_5)_3\text{SnCl} \rightarrow 3\text{-[(C}_6\text{H}_5)_3\text{Sn]C}_5\text{H}_4\text{N} + \text{LiCl} \quad [2]$$

$$3\text{-[(C}_6\text{H}_5)_3\text{Sn]C}_5\text{H}_4\text{N} + \text{CH}_3\text{I} \rightarrow \{3\text{-[(C}_6\text{H}_5)_3\text{Sn]C}_5\text{H}_4\text{NCH}_3\}^+\text{I}^- \quad [3]$$

Spectral data for both (**I**) and (**II**) are entirely consistent with their proposed formulations, and 78 K Mössbauer spectroscopic data for (**I**) (IS = 1.25, QS = 0.00 mm s^{-1}) are identical (within estimated errors) to those measured previously for 4-(triphenylstannyl)pyridine (IS = 1.28, QS = 0.00 mm s^{-1}).[22] Interestingly, while the electronegativities of C_6H_5 and C_5H_4N are sufficiently similar to maintain a charge distribution of cubic symmetry about tin, i.e. zero quadrupolar splitting, the Mössbauer spectrum of the pyridinium salt (**II**) is best fit to a doublet (QS = 0.51 mm s^{-1}, $\chi^2 = 475$ for 512 channels) rather than a singlet ($\chi^2 = 705$). Evidently, the quaternary nitrogen cation promotes electron withdrawal from the nearby Sn-C bond significantly more effectively than the C_6H_5 groups, thereby generating a measurable electric field gradient at tin, as has previously been noted for $(CH_3)_3SnC_5H_4N$, but not in the case of 4-$[(C_6H_5)_3Sn]C_5H_4NO$.[22]

Tin analysis of (**III**) shows that the cation exchange process yields a phyllosilicate with organotin-substituted pyridinium cations occupying 40% of the cation exchange sites. The presence of (**II**) in the interlamellar region is confirmed by an increase in the d(001) spacing from 12.6 Å, for the monolayer hydrate of the Na$^+$-montmorillonite, to 19.1 Å. Dehydration of (**III**) under vacuum (16 h at 10^{-2} mm Hg) at room temperature (20°C) decreases the latter to 17.7 Å, corresponding to a gallery height (Δd) of 8.1 Å. These changes are shown schematically in Fig. 1. However, due to the microcrystalline nature of the montmorillonite, a 3-dimensional X-ray analysis is not possible and, therefore, the exact position of the water molecules in the hydrated form of (**III**) cannot be determined. Nevertheless, a change in basal spacing due to the presence or absence of extra-coordination sphere water is not uncommon and has been reported on several occasions, e.g. in pyridine saturated Na$^+$-montmorillonite[23, 24] and in $(C_{18}H_{37})_2(CH_3)_2N^+$-exchanged clays.[25]

Using the available crystallographic data for $(C_6H_5)_4Sn$,[26] we calculate that this molecule, including C—H groups, can be described by a cube of dimensions 6.995 Å (Fig. 2). For $(3\text{-}CH_3C_6H_4)_4Sn$,[27] the cube is of side 6.953 Å based upon the hydrogen on C(4) which is marginally further from tin than any of the methyl hydrogens. These values indicate that a cube of ca. 7.0 Å can be used to describe (**II**) and will represent the minimum gallery height that this cation can achieve. The observed gallery height of 8.1 Å is in good agreement with this analysis, and suggests that reasonable predictions of the spacing ability of these simple, spherically symmetrical cations are possible

In addition to characterising the structure and bonding within the free cation, Mössbauer spectroscopy can also be used as a post-exchange probe of the environment of tin in the interlayer space of the montmorillonite. The Mössbauer

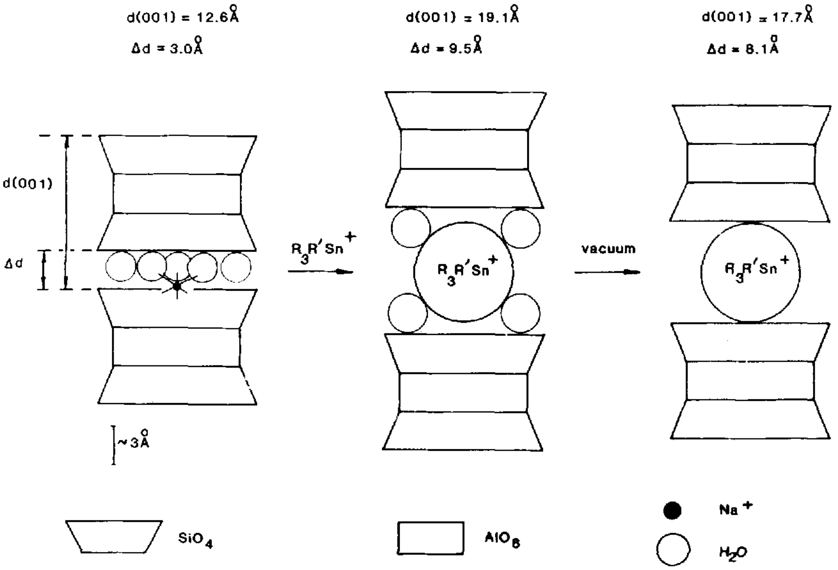

Figure 1 Schematic representation of the exchange of sodium montmorillonite with *N*-methyl-3-(triphenylstannyl)pyridinium cations. A net negative charge on the layers arises from Fe^{2+}, Mg^{2+} sites in the AlO_6 octahedral layer.

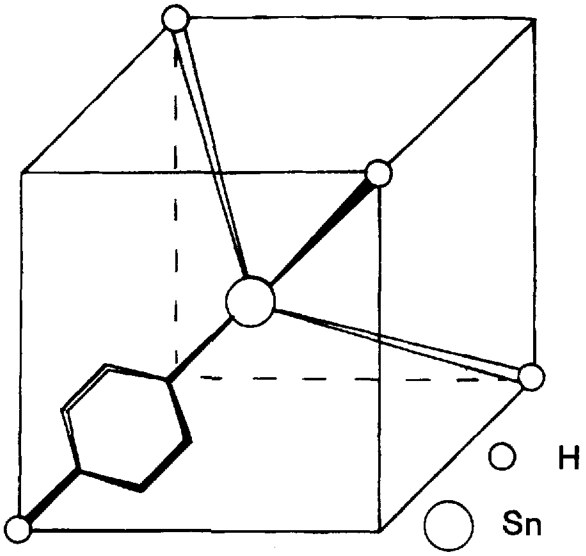

Figure 2 *Cubic representation of the space filling capacity of* tetraorganotins. For three of the aromatic groups, only the H(4) atoms are included for clarity.

data for the hydrated, cation exchanged clay (**III**) fit well to a simple doublet ($\chi^2 = 509$), with parameters (IS = 1.29, QS = 0.85 mm s^{-1}) very similar to those of the cation before intercalation. This is good evidence that a unique tin environment is present in the clay, at least within the limits of resolution of the Mössbauer experiment, and that the integrity of the cation is maintained during the exchange process. This latter point is important because several workers have reported that the *partially* hydrated Na^+-cation in the clay interlayer is sufficiently acidic to protonate detectable amounts of tetraphenylporphyrin (TTP),[28] or to demetallate and protonate weak metallocomplexes such as Fe(III)TPP.[29] Unfortunately, it was not possible to analyse the vacuum dried sample in the completely dehydrated state by thermogravimetry due to the difficulty of evacuating the balance, and hence the sample in situ. Thus, during the 1–2 min required to transfer the sample from the vacuum system to the thermobalance exposure to atmospheric moisture occurs, and is sufficient to cause significant rehydration of clays in general and this pillared clay in particular. Consequently, it was allowed to fully rehydrate at room temperature (20°C) and humidity (50%) prior to recording the thermogram. Since the thermogravimetric traces for the air dried and rehydrated samples of (**III**) were virtually identical within experimental error (Fig. 3), it may be concluded that (**III**) is resistant to the acid nature of the clay under the conditions utilised here. The enhanced electric field gradient at tin in (**III**) could arise either from a physical distortion of bond angles between the metal and ligating atoms brought about either by the 'sandwiching' effect of aluminosilicate sheets

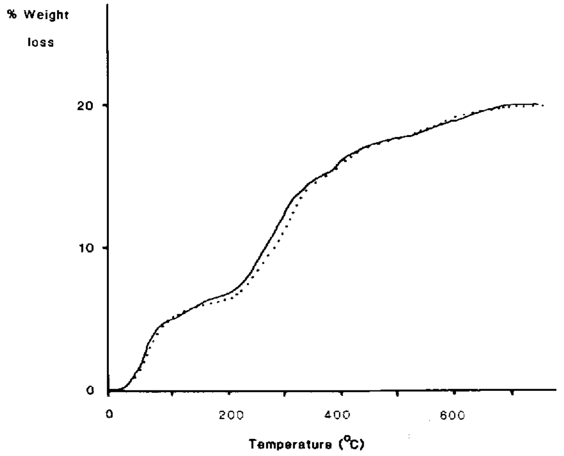

Figure 3 Thermogravimetric curves for the air dried (——) and rehydrated (····) forms of (**III**). See text for details.

or by the presence of interlayer water molecules (hence lowering the symmetry about the tin), or by a change in the electronegativity of the $[C_5H_4NCH_3]^+$ group by ion-pairing between anionic layers and the pyridinium cation. Such rationale are, at present, merely speculations.

Furthermore, Mössbauer spectra measured over a range of temperatures can give information regarding the tightness of binding of the tin within the solid lattice. Since:

$$A(T) \propto f(T) = \exp \frac{-\langle x(T)^2 \rangle}{\lambda^2} \qquad [4]$$

$$\frac{dA(T)}{dT} = \frac{d}{dT}\exp(-6E_R T/k\theta_D^2) \qquad [5]$$

where $A(T)$ is the area under the spectral envelope at temperature T, f the recoil-free fraction, $\langle x(T)^2 \rangle$ the mean square amplitude of vibration of the Mössbauer atom, λ the wavelength of the Mössbauer transition divided by 2π, E_R the Mössbauer recoil energy and θ_D the Debye temperature for the lattice, plots of $\ln[A(T)/A(78)]$ vs T are linear. Normalisation of the data to 78 K is merely to facilitate intersample comparison. The slope of these plots, $\mathbf{a} = -d\ln A/dT$, is characteristic of the rigidity of the lattice as felt by the Mössbauer atom, with more rigid lattices having smaller **a** values.[20] Variable temperature Mössbauer spectroscopic (v.t.M.s.) data for (**II**) and (**III**) are given in Fig. 4. For (**II**), $\mathbf{a} = 1.56 \times 10^{-2}\,K^{-1}$ (78–145 K, 8 pts, correlation coefficient $r = -0.998$), a result which is in good agreement with that found for $4\text{-}[(C_6H_5)_3Sn]C_5H_4N$ ($10^2\mathbf{a} = 1.66\,K^{-1}$)[22] as expected from the near equality of the vibrating masses, and a result which is typical of discrete molecular units within the solid lattice. Upon intercalation, the vibrational freedom of the tin is reduced ($10^2\mathbf{a} = 1.28\,K^{-1}$; 78–225 K, 18 pts, $r = -0.999$) and can be related to the sandwiching effect of the aluminosilicate layers, and is thus diagnostic of the intercalation process.

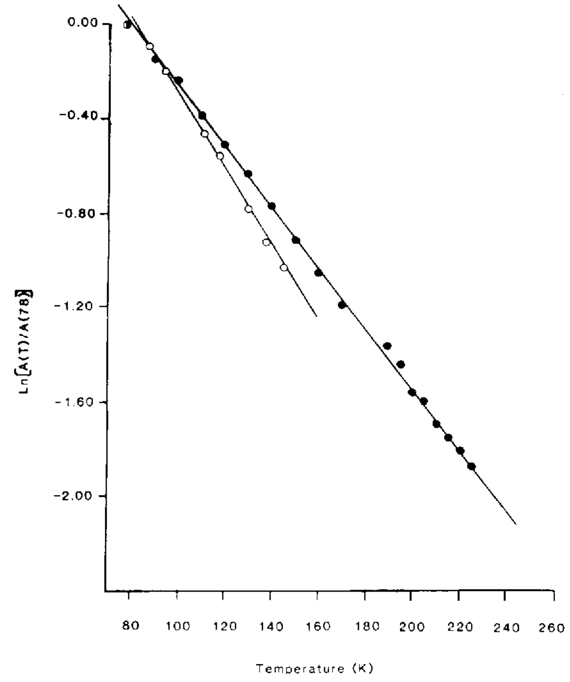

Figure 4 Variable-temperature ^{119}Sn Mössbauer spectroscopic data for (○; **II**) and (●; **III**).

The use of v.t.M.s. to probe the interlayer region of suitably-exchanged phyllosilicate minerals is, to our knowledge, limited. Diamant et al.[30] have used the technique to distinguish structural and exchanged Fe(II, III), and, in particular, have made use of a discontinuity at ca. 210 K in the $\ln A$ vs T plot for Fe^{2+}-exchanged montmorillonite as evidence for interlayer rather than structural iron in this system. The discontinuity arises from the onset of local, large vibrational amplitudes of interlayer water molecules which are in close proximity (including direct bonding) to the cation, and which are known from calorimetry[31] and n.m.r.[32,33] studies to commence near this temperature. In the case of (**III**), no such discontinuity occurs in the $\ln A$ vs T plot (Fig. 4) and is consistent with the hydrophobic nature of the ligands bonded to tin. Thus, the enhanced vibrational freedom enjoyed by Fe^{2+} at $T > 210$ K resulting from greater mobility of the interlayer water molecules is negated by the intervening aryl groups in the case of (**III**). These results underline the value of Mössbauer spectroscopy, in both the single and variable temperature forms of the experiment, as a probe of the environment of active interlayer cations.

CONCLUSIONS

These results show that high-spacing phyllosilicate materials can be achieved using organometallic cation pillars. Furthermore, the fact that only ca. 40% of the exchange sites are occupied by pillar cations means that further exchange with catalytically active M^{3+} cations ($M = Al, Cr, Fe$) is, in principle, possible. The gallery height of the clay in the current study compares favourably with those produced using poly-(oxymetal) cations,[5] niobium and tantalum clusters $M_6Cl_{12}{}^{n+}$, $n = 1, 2$[34] and metal carbonyls with phosphonium ligands as interlayer cations[10] which maximise at ca. 9 Å, but at 8.1 Å, is not exceptional. However, it does demonstrate the validity of our approach to the tailoring of the interlayer space. In addition to variations in gallery height, the porosity of the material can be manipulated by sequential increases in the cation charge, e.g. $[(C_6H_5)_nSn(C_5H_4NCH_3)_{4-n}]^{(4-n)+}$ ($n = 3, 2, 1, 0$) which ultimately controls the extent of cation loading. Variations in the central metal add a further dimension to the versatility of the systems. It would thus appear possible to produce catalytically active phyllosilicate materials, with different catalytic agents, in which additional organometallic pillars are used to engineer the spatial accessibility of the catalyst and hence maximise its size/shape/stereochemical selectivity. Our current efforts are directed towards realising this goal.

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REFERENCES

1. Barrer, RM *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978, pp 453–475
2. Endo, T, Mortland, MM and Pinnavaia, TJ *Clays and Clay Minerals*, 1980, 28: 105
3. Endo, T, Mortland, MM and Pinnavaia, TJ *Clays and Clay Minerals*, 1981, 29: 153
4. Manos, CG, Mortland, MM and Pinnavaia, TJ *Clays and Clay Minerals*, 1984, 32: 93
5. Vaughan DEW and Lussier, RJ Preparation of molecular sieves based on pillared interlayered clays (PILC). In: *Proc. 5th Internat. Conf. Zeolites, Naples, 1980*, Rees, LDC (ed), Heyden, London, 1980, pp 94–101
6. Traynor, MF, Mortland, MM and Pinnavaia, TJ *Clays and Clay Minerals*, 1978, 26: 318
7. Loeppert, RH, Jr, Mortland, MM and Pinnavaia, TJ *Clay and Clay Minerals*, 1979, 27: 201
8. Pinnavaia, TJ, Rayatha, R, Lee, JGS, Halloran, LJ and Hoffman, JF *J. Am. Chem. Soc.*, 1979, 101: 6891
9. Farzaneh, F and Pinnavaia, TJ *Inorg. Chem.*, 1983, 22: 2216
10. Rayatha, R and Pinnavaia, TJ *J. Catal.*, 1983, 80: 47
11. Ballantine, JA, Purnell, H, Rayanakorn, M, Thomas, JM and Williams, KJ *J. Chem. Soc., Chem. Commun.*, 1981, 427
12. Adams, JM, Bylina, A and Graham, SH *J. Catal.*, 1982, 75: 190
13. Gregory, R, Smith, DJH and Westlake, DJ *Clay Minerals*, 1983, 18: 431
14. Atkins, MP, Smith, DJH and Westlake, DJ *Clay Minerals*, 1983, 18: 423
15. Adams, JM, Clement, D and Graham, SH *Clays and Clay Minerals*, 1983, 30: 19
16. Adams, JM, Clement, D and Graham, SH *J. Chem. Res.(S)*, 1981, 254
17. Occelli, ML *Ind. Eng. Chem. Prod. Res. Dev.*, 1983, 22: 553
18. Bennet, H and Reed, RA *Chemical Methods of Silicate Analysis*, Academic Press, London, 1971, pp 71–79
19. Adams, JM, Reid, PI and Walters, MJ *Sch. Sci. Rev.*, 1977, 59: 722
20. Molloy, KC and Quill, K *J. Chem. Soc., Dalton Trans.*, 1985, 1417
21. Gilman, H and Goreau, TN *J. Org. Chem.*, 1952, 17: 1470
22. Phillips, JE and Herber, RH *J. Org. Chem.*, 1984, 268: 39
23. Adams, JM, Thomas, JM and Walters, MJ *J. Chem. Soc., Dalton Trans.*, 1975, 1459
24. Adams, JM and Breen, C *J. Colloid Interface Sci.*, 1982, 89: 272
25. Jones, TR *Clay Minerals*, 1983, 18: 399
26. Chieh, PC and Trotter, J *J. Chem. Soc. (A)*, 1970, 911
27. Karpidesw, A and Oertel, M *Acta Crystallogr.*, 1977, B33: 683
28. Cady, SS and Pinnavaia, TJ *Inorg. Chem.*, 1978, 17: 1501
29. van Damme, H, Crespin, M, Obrecht, F, Cruz, MI and Fripiat, JJ *J. Colloid Interface Sci.*, 1978, 66: 43

30. Diamant, A, Pasternak, M and Banin, A *Clays and Clay Minerals*, 1982, 30: 63

31. Anderson, DM and Tice, AR *Soil Sci. Soc. Amer. Proc.*, 1971, 35: 47

32. Blaine, RL Proton magnetic resonance in clay minerals, *Natl. Acad. Sci. Natl. Res. Council*, Publication 859, 1961, pp 44–55

33. Hecht, AM, Dupont, M and Ducros, P *Bull. Soc. Franc. Miner. Crist.*, 1966, LXXXIX: 6

34. Christiano, SP, Wang, J and Pinnavaia, TJ *Inorg. Chem.*, 1985, 24: 1222