Zeolitic behaviour in stuffed silica polymorphs

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Alkali-metal aluminosilicates with the quartz, cristobalite and tridymite structures possess zeolitic behaviour when imperfectly crystallised. In aqueous solution these novel materials display a level of cation exchange which is comparable with synthetic zeolites. In contrast, when they are well crystallised these stuffed silica polymorphs, as they are also known, do not possess this cation exchange behaviour. They can be prepared simply from clay minerals and have potential as inexpensive inorganic cation exchangers.

The challenge of turning clay minerals, which are very abundant, into zeolites, which are very valuable and useful as catalysts, adsorbents and ion exchangers, has tantalised materials scientists for almost fifty years. Numerous papers and patents have described the use of aluminosilicate clays as feedstock for aqueous or hydrothermal zeolite synthesis, where the clay is digested with subsequent nucleation of zeolite crystals. However, the slight cost advantage of using a naturally occurring source of aluminosilicate is usually more than offset by the disadvantage of chemical impurity introduced by the clay. Even where chemical purity and colour are less important, conventional zeolite synthesis from clays still entails rather complex and expensive industrial processes.

The present work describes the important discovery that zeolite-like inorganic cation exchange materials can be prepared by a one-step solid-state reaction process using aluminosilicate mineral starting materials. Reaction takes place under such mild conditions that the particle size and morphology of the mineral starting materials are completely preserved in the alkali-metal aluminosilicate product even though their composition and crystal structure have been radically altered.

The new alkali-metal aluminosilicate materials, which have structures based on the stuffed silica polymorphs,[1] have a high cation exchange capacity (CEC) in aqueous solution. The majority of interstitial alkali-metal cations are exchangeable and their selective cation exchange is comparable to zeolites.

The stuffed silica polymorphs: kalsilite, kaliophilite, nepheline, carnegieite and eucryptite, have the same framework structures as the three principal crystalline polymorphs of SiO_2, tridymite, cristobalite and quartz. These silica polymorphs have simple three-dimensional corner-connected tetrahedral frameworks which are charge neutral. The stuffed silica polymorphs, with ideal composition $MAlSiO_4$ ($M = Li$, Na, K), have frameworks where half of the silicon cations are replaced by aluminium cations, resulting in a net negative charge for the framework. Alkali-metal cations provide the charge balance ($Si^{4+} \leftrightarrow Al^{3+} + M^+$, $M = Li$, Na, K) in these structures and occupy the interstices in the respective frameworks [see Fig. 1(*a*)–(*c*)], hence the name.

Kalsilite and its closely related superstructure phase kaliophilite have ideal composition $KAlSiO_4$, while nepheline exists as a solid solution and has the composition $Na_{4-x}K_xAl_4Si_4O_{16}(0 \leqslant x \leqslant 1)$. All of these minerals have tridymite-type crystal structures. Carnegieite with ideal composition $NaAlSiO_4$ has a cristobalite-type crystal structure, whereas eucryptite with ideal composition $LiAlSiO_4$ has a crystal structure closely related to that of quartz.

There are several similarities between the stuffed silica polymorphs and zeolites. They are tectosilicates and, apart from water content, their chemical compositions are similar, *e.g.* anhydrous Na zeolite A has the same composition as carnegieite, $NaAlSiO_4$. It can be argued that, in terms of their structure, the stuffed silica polymorphs are the simplest members of the zeolite family. They comprise six-membered rings of tetrahedra as their secondary building unit (SBU).[2] However, the principal reason for their non-inclusion as zeolites is that they are not porous and that the interstitial alkali-metal cations are not exchangeable under readily accessible conditions, *i.e.* in aqueous salt solution at atmospheric pressure from room temperature up to *ca.* 100 °C.

This is not to say that the interstitial cations of these materials cannot be exchanged. The interstitial cations of kalsilite and related aluminosilicates have been exchanged by treating the material at high temperature and pressure under hydrothermal conditions[3] and similar exchange of cations was observed following treatment with molten salts such as MNO_3 or MCl ($M = Li$, Na, K, Ag).[4] Other workers[5] have exchanged the interstitial Na^+ cation of carnegieite with Li^+ by treatment with molten $LiNO_3$. It has also been reported that, while it is not possible to substitute Li^+ in β-eucryptite by treatment using molten salts with bigger cations such as Na^+, K^+ or Ag^+, exchange by divalent cations Cu^{2+} and Mn^{2+} was relatively straightforward under such conditions.[6]

Associated with this ability to exchange cations by treatment with molten salts is the property of ionic conductivity of the interstitial alkali-metal cations observed for carnegieite and related materials,[7–9] though by comparison with other solid electrolytes, *e.g.* β- and β″-aluminas, their cationic conductivity is relatively low.

Even though interstitial cations in aluminosilicates with the stuffed silica polymorph structures are exchangeable when treated with molten salts, it is generally acknowledged that these materials have negligible CEC associated with the bulk structure, either in aqueous solution or in organic solvents. However, the cation exchange behaviour of these materials is quite dramatically different when they are imperfectly crystalline.

Synthesis

Imperfectly crystallised stuffed silica polymorphs with zeolitic cation exchange properties can be prepared by various synthetic routes. The key to successful synthesis is the use of reactive starting materials, that is, components or component precursors which facilitate reaction at relatively low temperatures. More rigorous conditions normally associated with the formation of carnegieite and related aluminosilicates, *e.g.* annealing oxide components at ⩾1000 °C overnight, result in the formation of well crystallised and/or perfectly ordered materials which tend not to display aqueous cation exchange.

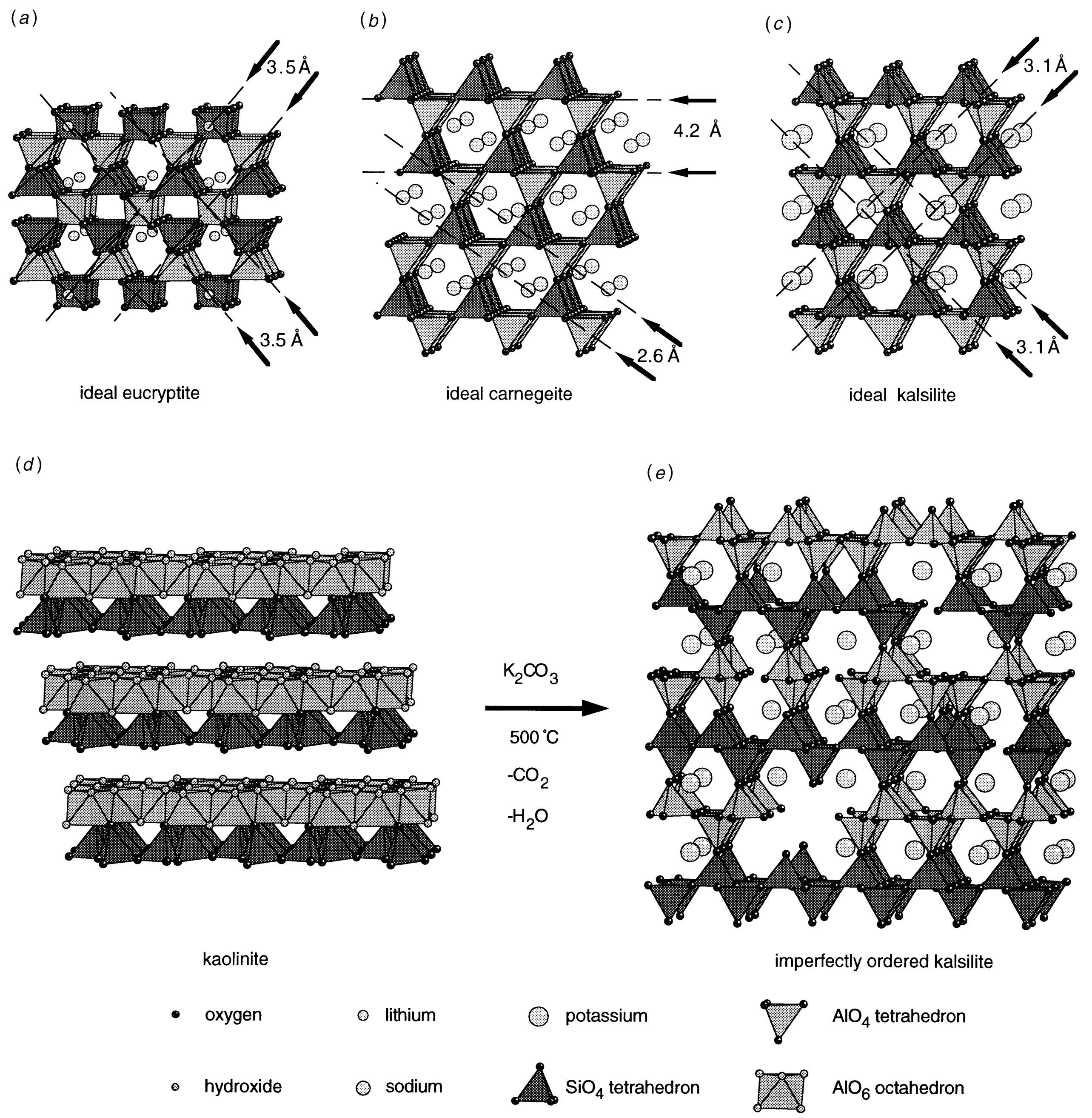

Fig. 1 Schematic polyhedral representation of (*a*) ideal eucryptite, (*b*) ideal carnegieite, (*c*) ideal kalsilite, (*d*) kaolinite and (*e*) the proposed model for the zeolite-like imperfectly crystalline kalsilite. The ideal stuffed silica polymorphs show exact silicon:aluminium ordering whereas the imperfectly crystalline materials have inherited the alternating layers of silicate and aluminate from the kaolinite. Both ideal and imperfectly crystalline kalsilite possess layers of interstitial and framework cations which give rise to the strong peak at *ca.* 3.1 Å in their XRD profiles. A similar commonality is observed for carnegieite, nepheline and eucryptite.

To achieve relatively mild reaction conditions, an aluminosilicate mineral starting material is used which, by definition, contains aluminium and silicon cations mixed on the atomic level, *i.e.* on the nanometre scale. Aluminosilicate phyllosilicates, such as the kaolin group clay minerals with Al : Si ratio of 1 : 1 and pyrophyllite with Al : Si ratio of 1 : 2, are particularly suitable due to their relative chemical purity. While aluminosilicate phyllosilicate compositions represent a wide range of Si : Al ratios, imperfectly crystallised stuffed silica polymorphs can be formed from all of them provided there is sufficient alkali-metal oxide containing reagent to balance the charge of aluminium present in the mineral. Various soluble alkali-metal salts and hydroxides can provide the source of the alkali-metal cations, provided they decompose upon heating to *ca.* 1000 °C to give alkali-metal oxide. This requirement precludes alkali-metal halides and sulfides. The specific conditions of synthesis of the three imperfectly crystallised stuffed silica polymorphs described in detail in the present work are given below.

The potassium aluminosilicate was prepared by dispersing 2 kg of a well crystallised kaolinite from Skardon River, Australia, in 4.7 l of water. A solution containing 0.92 kg of commercial grade K_2CO_3 in 3.5 l of water was slowly added and the resultant slurry stirred vigorously for 20 min. The slurry was then dehydrated using a spray drier with an inlet temperature of 250 °C. The spray-dried reaction mixture was then heated at 500 °C for 3.5 h. Sodium aluminosilicate was prepared similarly by dispersing 1 kg of the same kaolinite in 2.33 l of water. A solution containing 0.365 kg of commercial grade Na_2CO_3 in 1 l of water was slowly added and the resultant slurry stirred vigorously, again for 20 min. The slurry was then dehydrated and reacted using the same procedure and conditions as for the potassium material. Lithium aluminosilicate was prepared similarly by dispersing 200 g of the same kaolinite in 470 ml of water. A solution containing 134 g of AR grade lithium acetate dihydrate in 350 ml of water was slowly added and the resultant slurry stirred vigorously for 30 min. The slurry was then dehydrated and reacted using the same procedure and conditions as for the potassium and sodium materials, except that the dried mixture was heated for 16 h.

These materials could also be formed *via* a gel synthesis route using synthetic reagents such as soluble alkali-metal silicates and colloidal silica, in combination with reactive forms of alumina, such as aluminium nitrate nonahydrate, though the scale of mixing of aluminium and silicon at the outset is not at the atomic level, as achieved using aluminosilicate mineral starting materials. Nonetheless, alkali-metal aluminosilicates with the same structure and properties as those obtained using mineral starting materials could be obtained from synthetic reagents.

The synthesis of well crystallised carnegieite from various forms of kaolinite (ordered, disordered and decomposed) in reaction with sodium carbonate,[10] by thermal decomposition of Na zeolite A,[11–13] and by other methods using aluminosilicic gel or sodium silicate glass[10] have previously been reported. However, none of these authors focussed on the imperfectly crystalline reaction product, nor did they test their materials for cation exchange properties.

Characterisation

The structures of the various subject materials are characterised most definitively by a combination of X-ray powder diffraction and solid-state NMR spectroscopy.

The X-ray powder diffraction profiles (Fig. 2) display broad diffraction peaks characteristic of protocrystalline stuffed silica polymorphs. The diffraction profile in each case is primarily dependent on the interstitial alkali metal, M. While at first glance one might be tempted to describe the materials as 'amorphous', comparison of the broad diffraction peaks with those of the same materials annealed at higher temperatures to promote longer-range order shows that the principal periodicities associated with the well crystallised phases are observable in the diffraction patterns of the poorly ordered materials.

The XRD profile of the potassium aluminosilicate material comprises a single very broad diffraction peak [Fig. 2(*a*)] which corresponds to the 102 reflection ($d = 3.12$ Å) in kalsilite.[14] This broad peak indicates that, while other long-range ordering is absent in this poorly crystalline material, there is still periodic structure (protocrystallinity) associated with the layers of interstitial and framework cations [refer to 3.1 Å layers indicated by dashed lines in Fig. 1(*c*)]. A similar interpretation is given to the XRD profile of the sodium aluminosilicate which comprises a composite of several overlapping broad diffraction peaks [Fig. 2(*c*)], corresponding to the 111 ($d = 4.2$ Å) and 220 ($d = 2.6$ Å) peaks of high-carnegieite[15] [refer to 4.2 and 2.6 Å layers indicated by dashed lines in Fig. 1(*b*)] and the principal diffraction peaks of nepheline,[16] most notably the 201 reflection at $d = 3.03$ Å, analogous to the 3.12 Å peak in kalsilite. These broad peaks relate to the layers of interstitial and framework cations in carnegieite and nepheline. The lithium aluminosilicate XRD profile comprises a single broad diffraction peak [Fig. 2(*e*)] which is associated with the layers of interstitial and framework cations [refer to 3.5 Å layers indicated by dashed lines in Fig. 1(*a*)] in high-eucryptite[17] corresponding to the 102 ($d = 3.52$ Å) peak. Only the 'before' and 'after' XRD profiles are presented here, but the transformation takes place progressively with increase in annealing temperature.

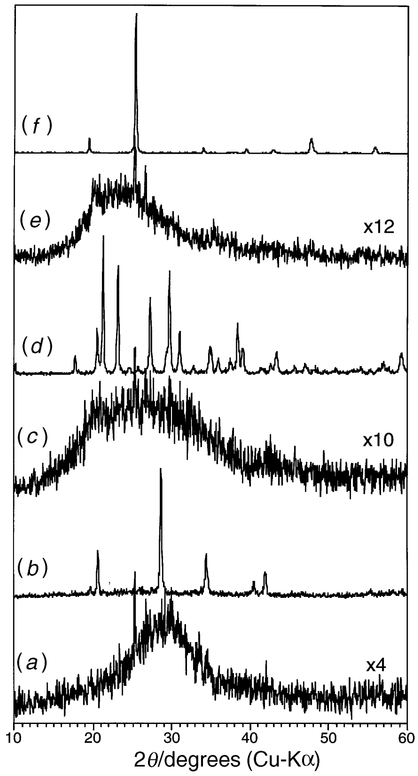

Fig. 2 XRD profiles of (*a*) imperfectly crystalline kalsilite-related material prepared from a slurry of kaolinite and K_2CO_3, dried then heated at 500 °C for 3.5 h; (*b*) well crystallised kalsilite prepared by further heating at 1000 °C for 16 h; (*c*) imperfectly crystalline carnegieite/nepheline-related material prepared from a slurry of kaolinite and Na_2CO_3, dried then heated at 500 °C for 3.5 h; (*d*) a mixture of well crystallised nepheline and carnegieite prepared by further heating at 900 °C for 16 h; (*e*) imperfectly crystalline eucryptite-related material prepared from a slurry of kaolinite and lithium acetate dihydrate, dried then heated at 500 °C for 16 h; (*f*) well crystallised eucryptite prepared by further heating at 1000 °C for 16 h

Confirmation that these imperfectly ordered materials have the structures of the stuffed silica polymorphs, *i.e.* they are tectosilicates, is obtained from solid-state ^{27}Al NMR. ^{27}Al NMR chemical shift is sensitive to whether the aluminium is four-, five- or six-coordinated,[18] and the ^{27}Al signal for each occurs at δ *ca.* 57, in the range δ 50–80 which is characteristic of tetrahedrally coordinated aluminium. The ^{27}Al MAS NMR spectrum of the 500 °C potassium aluminosilicate material is compared with that of the kaolinite starting material in Fig. 3. In kaolinite the aluminium is octahedrally coordinated, so the absence of any significant octahedrally coordinated aluminium supports the interpretation of the XRD data that these materials have reacted completely and are essentially tectosilicates.

In framework aluminosilicates such as zeolites and feldspars, ^{29}Si NMR can be used to determine the next-nearest neighbour coordination environment of the silicon atoms in the structure, *i.e.* Q_4 Si(*n*Al) $0 \leqslant n \leqslant 4$.[19,20] In well crystallised carnegieite a single resonance at δ 81.8 (relative to TMS) is observed corresponding to Si(4Al),[21] or exact Si : Al ordering. Fig. 4 shows the ^{29}Si MAS NMR spectra of the kaolinite starting material and the potassium aluminosilicate materials annealed at 500 and 1000 °C as described in Fig. 2. The sharp doublet characteristic of well- crystallised kaolinite gives way to a single broad resonance at δ 88.5 (FWHM = 16 ppm) observed for the imperfectly crystalline kalsilite-related material suggests a range of Q_4 environments but that little, if any, silicon occurs in Si(0Al) and Si(1Al) environments. Annealing at 1000 °C promotes the exact Si : Al ordering to give a sharper, but slightly asymmetric signal at δ −87.2 (FWHM = 8 ppm) corresponding to a predominance of Si(4Al) environments.

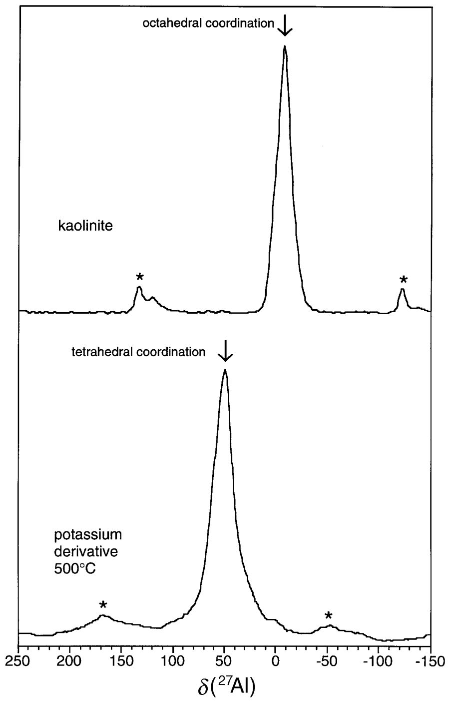

Fig. 3 ^{27}Al MAS NMR spectrum of imperfectly crystalline potassium aluminosilicate material annealed at 500 °C, as described in Fig. 2 caption, juxtaposed with the spectrum for the kaolinite starting material. Spectra were collected on a Bruker MSL400 spectrometer at 104.228 MHz with a sample spinning speed of 11.4 kHz and a recycle time of 1 s.

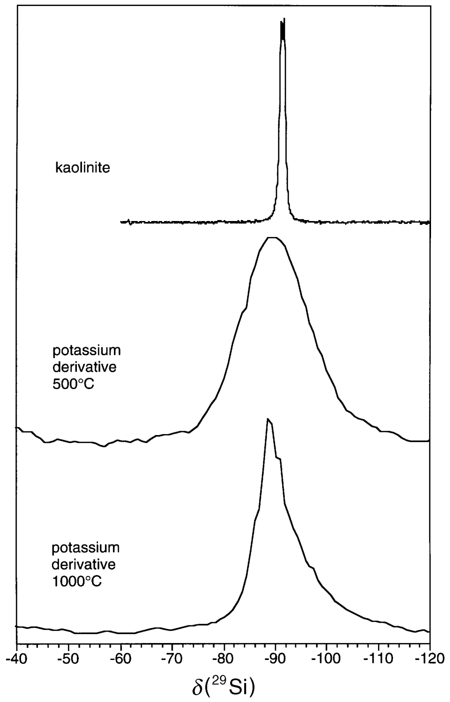

Fig. 4 ^{29}Si MAS NMR spectra of potassium aluminosilicate material prepared as described in Fig. 2 caption annealed at 500 °C (*a*) and 1000 °C (*b*), collected on a Bruker MSL400 instrument at 79.468 MHz. A sample spinning speed of 4.3 kHz was used with a recycle time of 2 s. The spectrum of kaolinite starting material is included for comparison.

The morphology, specific surface and particle size distribution of imperfectly crystallised stuffed silica polymorphs is very dependent on the starting materials. The use of such mild reaction conditions for the solid-state reaction tends to leave these properties unchanged, despite there being a complete change in crystal structure and composition. Fig. 5(*a*) and (*b*) show scanning electron micrographs (secondary electron image) at two different magnifications of the sodium aluminosilicate material of approximate composition $NaAlSiO_4$ prepared from kaolinite at 500 °C. Remarkably the reaction product appears identical to the kaolinite used in this particular reaction. The same holds true for other aluminosilicate phyllosilicate mineral starting materials.

Cation exchange properties

The imperfectly crystalline stuffed silica polymorphs described above display cation exchange behaviour quite similar to that of zeolites. Table 1 presents cation exchange data for a range of alkali-metal and divalent cations for the materials described in the Synthesis section and whose XRD profiles are shown in Fig. 2.

The trends in the alkali-metal cation exchange results (see Table 1) are consistent with our understanding of the structure

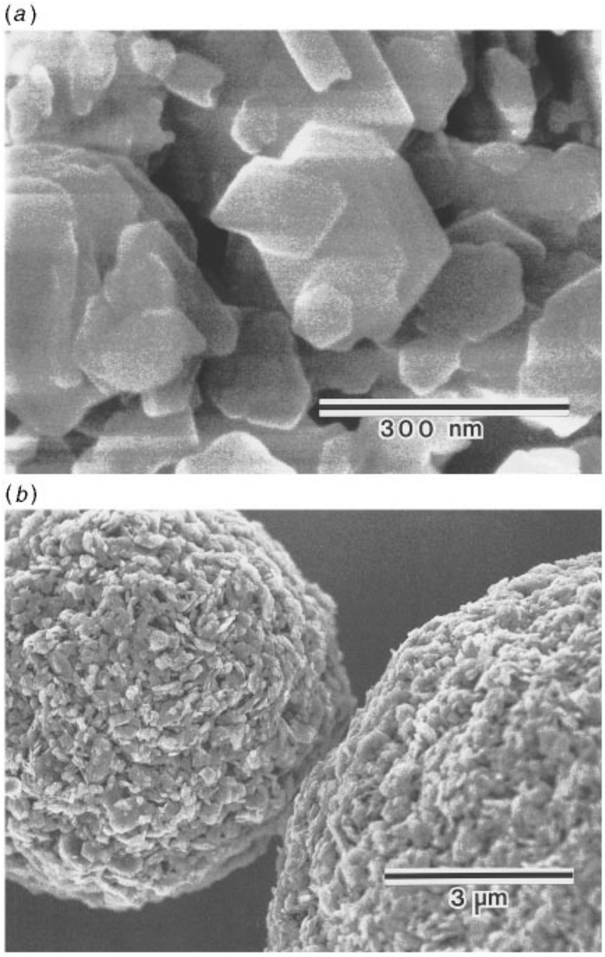

Fig. 5 Scanning electron micrographs (secondary electron images), at two different magnifications, of the sodium aluminosilicate material of approximate composition $NaAlSiO_4$ prepared from kaolinite by solid-state reaction at 500 °C, according to the method described in the Synthesis section. At low magnification (*b*) the spherical aggregates which result from spray-drying the reaction mixture are clearly seen. At higher magnification (*a*) the sodium aluminosilicate particles appear to have an almost identical pseudo-hexagonal plate-like morphology to the kaolinite starting material. The images were collected using a Hitachi Field Emission scanning electron microscope operating at 4 kV.

Table 1 Percentage cation exchange for imperfectly crystalline stuffed silica polymorphs[a]

			imperfectly crystalline stuffed silica polymorphs[c]			
exchange cation	T/°C	exchange[b] solution	Li	Na	K	Na zeolite A
Li	65	10 M $LiNO_3$	—	75	80	—
Na	65	10 M $NaNO_3$	58	—	86	—
K	65	10 M KNO_3	6	78	—	—
Mg	20	0.8 M $MgCl_2$	10	23	30	68
Mg	60	0.8 M $MgCl_2$	48	69	64	74
Ca	20	0.8 M $CaCl_2$	6	13	14	95[d]
Ca	60	0.8 M $CaCl_2$	12	33	41	94[d]
Zn	20	0.8 M $Zn(NO_3)_2$	38	45	56	100[d]
Cd	20	0.8 M $Cd(NO_3)_2$	34	28	35	98[d]
Cd	40	0.8 M $Cd(NO_3)_2$	20	39	44[d]	99[d]
Pb	20	0.8 M $Pb(NO_3)_2$	34	35	49[d]	100[d]
Pb	40	0.8 M $Pb(NO_3)_2$	36	59[d]	66	100[d]
			well crystallised stuffed silica polymorphs[c,e]			
			Li	Na	K	
Mg	60	0.8 M $MgCl_2$	4	5	5	—
Ca	60	0.8 M $CaCl_2$	<2	2	<2	—
Zn	20	0.8 M $Zn(NO_3)_2$	6	<2	<2	—
Cd	40	0.8 M $Cd(NO_3)_2$	<2	<2	<2	—
Pb	40	0.8 M $Pb(NO_3)_2$	4	2	2	—

[a] Determined directly by quantitative energy dispersive X-ray analysis as percentage reduction in interstitial alkali-metal content, except for $LiAlSiO_4$ where percentage increase in exchange cation was used due to the inability to analyse for Li. Percentages given as <2 indicate a result below the limit of detection within error. [b] 0.5 g of dispersed powder was stirred in 50 ml of solution overnight. $Cd(NO_3)_2$ and $Pb(NO_3)_2$ solutions were acidified with HNO_3 to *ca.* pH 4 to inhibit both complex formation in solution and precipitation of metal hydroxide once in contact with the exchange material. [c] Anhydrous stoichiometries as prepared are *ca.* $Li_{0.85}AlSiO_{3.925}$, $Na_{0.89}AlSiO_{3.945}$ and $K_{0.86}AlSiO_{3.93}$. 100% exchange is equivalent to *ca.* 690, 640 and 570 mequiv. $(100\ g)^{-1}$ respectively. 100% exchange for Na zeolite A is equivalent to *ca.* 700 mequiv. $(100\ g)^{-1}$. [d] The uptake of charge from the exchanging divalent cation exceeds the charge lost by the exchanged alkali-metal cation, presumably due to complex formation within the exchange material or surface precipitation of hydroxide. [e] Imperfectly crystalline stuffed silica polymorphs annealed at 1000 °C for 16 h.

of these imperfectly crystalline materials in that the exchange sites vary in size from the Li^+ site in eucryptite, the smallest, to the K^+ site in kalsilite, the largest. Consequently, there is a high level of exchange of Li^+ into the carnegieite (75%) and kalsilite (80%) materials, and only 6% exchange of K^+ into the eucryptite material. The characteristic XRD profiles for each of the materials do not change significantly upon exchange (see Fig. 6), confirming that the imperfectly crystalline aluminosilicate framework is essentially preserved in each case. There are nevertheless subtle changes to broad diffraction features which can be interpretted as due to the change in scattering power of the interstitial cations upon exchange.

Exchange data at various temperatures for the divalent cations Mg^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} are compared with those for Na zeolite A, a well studied inorganic cation exchange material, as well as the well crystallised stuffed silica polymorphs (Table 1). The exchange is expressed as percent exchange of the interstitial alkali-metal cation to facilitate comparison between materials of different formula mass. The conversion factors to the more familiar units mequiv. $(100\ g)^{-1}$ are given in the footnotes.

An important consideration in studying the cation exchange of these divalent cations, particularly Zn^{2+}, Cd^{2+} and Pb^{2+}, is the alkalinity of the exchange material. A 1% dispersion of the Na zeolite A used (Valfor 100, PQ Corporation) had an equilibrium pH of 10.5, compared with 9.5–10.0 for the imperfectly crystalline stuffed silica polymorphs. The equilibrium pH of the materials annealed at 1000 °C was lower again. To avoid, or at least minimise, surface precipitation of metal hydroxides due to their low solubility products, the exchange solutions for Cd and Pb were acidified with HNO_3 to *ca.* pH 4. Despite this, our analyses indicated that precipitation of hydroxide was a problem for Na zeolite A due to its intrinsic alkalinity,[22] but much less so for our less alkaline imperfectly crystalline stuffed silica polymorphs.

While the percentage exchangeability of the interstitial alkali-metal cations for the imperfectly crystalline materials is generally less than for Na zeolite A, except in the case of Mg^{2+} at 60 °C where the performance of the carnegieite and kalsilite materials is comparable, the proportion of exchangeable cations is still remarkably high, given that the well crystallised stuffed silica polymorphs have very few. The cation exchange also shows a temperature dependence in most cases.

Selective cation exchange is a commonly observed phenomenon for ion exchange materials and is driven principally by differences in electrostatic interaction between the exchanging cation and the ion exchange material framework.[23] Electrostatic interaction is stronger for cations of higher valence, smaller hydration sphere and higher polarisability. Selectivity can also be based on size, *i.e.* discrimination based on access to certain cation exchange sites, and is observed for Rb^+ and Cs^+ is some zeolites.[24]

Ion exchange isotherms for Zn^{2+} against Na^+ for sodium zeolite A and the sodium aluminosilicate material were identical, though this is not surprising given the similarities in chemistry, structure and ion exchange capacity. However, the kinetics of exchange for the alkali-metal aluminosilicate materials prepared from kaolinite (specific surface *ca.* 25 $m^2\ g^{-1}$) were generally more sluggish than for synthetic zeolites. The kinetics of exchange are likely to improve by using high specific surface aluminosilicate phyllosilicate starting materials such as bentonite (specific surface typically $>50\ m^2\ g^{-1}$) or ball-milled kaolinite, as for this reaction process the specific surface of the starting material is essentially preserved in the final product. The higher specific surface of the exchange material will provide on average a shorter diffusion path to the exchange site, thereby improving the kinetics.

Mechanism of formation: structural model

The zeolitic behaviour of alkali-metal aluminosilicates with the structures of the three principal crystalline forms of SiO_2,

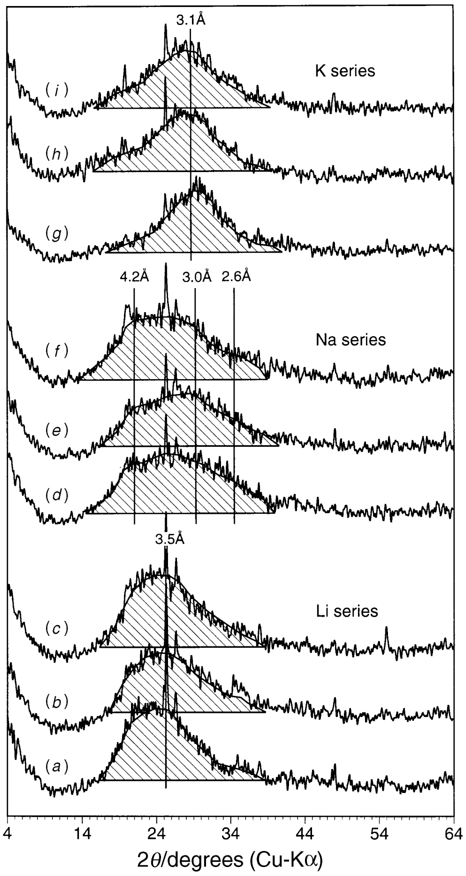

Fig. 6 XRD profiles of imperfectly crystalline alkali-metal aluminosilicate materials shown in Fig. 2 before and after exchange by other alkali-metal cations. Eucryptite-related lithium aluminosilicate (*a*) is compared with the same material after exchange by sodium (*b*) and potassium (*c*); carnegieite/nepheline-related sodium aluminosilicate (*d*) is compared with the same material after exchange by potassium (*e*) and lithium (*f*); kalsilite-related potassium aluminosilicate (*g*) is compared with the same material after exchange by lithium (*h*) and sodium (*i*). The conditions and level of exchange are given in Table 1.

when they are imperfectly crystallised, can be understood from consideration of how they might be formed from reactive starting materials such as aluminosilicate phyllosilicates.

Under the relatively mild reaction conditions used, the alkali-metal derived from the alkali-metal oxide containing salt diffuses into the aluminosilicate as the aluminosilicate dehydrates. There is no mass transport of aluminium or silicon, only of water and alkali metal. The silicate layers in the phyllosilicate already comprise 6-rings of corner-connected tetrahedra. By a quasi-topotactic rearrangement of the oxygen atoms in the phyllosilicate, a stuffed silica polymorph aluminosilicate framework results. Which framework forms depends on which alkali metal occupies the interstices. The XRD profiles at the earliest stage suggest that the interstitial cation array is in place at the outset, and that the framework becomes increasingly ordered with further annealing.

The ^{29}Si NMR spectra suggest that the stuffed silica polymorph framework is initially formed with a minimum of rearrangement of the silicon and aluminium atoms from the starting material. This accords with the broad signal covering a range of Si(*n*Al) environments. It is only with further annealing that there is a tendency to Si : Al ordering.

The bulk cation exchangeability of these materials is attributed to the imperfection of the framework structure. While the interstitial cation array and most of the framework cations are in place, the structure must be full of defects to explain the cation exchange property. To use the analogy with zeolites, the chambers in the stuffed silica polymorph structures where the interstitial cations reside must be accessible.

Fig. 1(*d*) and (*e*) illustrates the proposed mechanism of formation of the imperfectly crystalline stuffed silica polymorphs from the clay mineral kaolinite. The chambers are essentially those of the stuffed silica polymorphs and increase in size from eucryptite to carnegieite to kalsilite, in keeping with the increasing ionic radius of the interstitial cations, Li^+, Na^+ and K^+. The channels or tunnels, which are non-existent in the ideal materials (the 6-rings in the stuffed silica polymorphs do not appear to allow ion exchange in aqueous solution), result from the defects in the three-dimensional framework.

As the imperfectly crystalline stuffed silica polymorphs are based on a tetrahedral aluminosilicate rather than a pure silicate framework, terminal OH groups are not required for charge balance, as would be expected from high-temperature solid-state synthesis. However, the observed equilibrium pH for these materials does suggest a degree of hydrolysis once in contact with aqueous solution.

The defects in the three-dimensional framework must be endemic in the structure to explain the bulk cation exchangeability in the 50–100 nm thick platelets observed in Fig. 5(*a*). It is not surprising, though, that diffusion through this imperfect framework might be significantly slower than in zeolites which typically possess a perfectly regular array of open tunnels and larger internal pore space. Unlike zeolites, imperfectly crystalline stuffed silica polymorphs possess no measurable internal surface. This together with very low mass loss on firing at 1000 °C, typically less than 2 mass% which is at least partly attributable to external surface adsorption, support the proposed model.

Without the intimate mixing of aluminium and silicon afforded by the use of aluminosilicate phyllosilicate minerals as starting materials, it would not be possible to generate imperfectly crystalline stuffed silica polymorphs with uniform structure and properties. The use of oxides or oxide precursors to produce the stuffed silica polymorphs in single phase requires temperatures in excess of 1000 °C, at which temperatures both loss of alkali-metal and irreversible vitrification can cause problems. Achieving thermodynamic equilibrium in alkali-metal silicate containing systems can be rather elusive depending on the synthetic route, the existence of window glass attests to that. And when crystalline phases are achieved, the stuffed silica polymorphs formed by conventional ceramic methods generally are well crystallised and display negligible CEC.

If there is a lesson to be learnt from these results it is that one should not dismiss as ‘amorphous’ materials that do not display long-range order as observable by XRD. Aluminosilicate phyllosilicates can be considered as highly reactive naturally occurring starting materials in abundant supply. With a little imagination and suspension of prejudice as to what comprises a reaction product, other new materials are likely to be discovered using a similar synthesis strategy.

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References

1 M. J. Buerger, *Am. Mineral.*, 1954, **39**, 600.
2 W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, Butterworth-Heinemann, Sydney, 3rd edn., 1992.
3 J. Roux, *C. R. Acad. Sci., Ser. D*, 1971, **272**, 3225.

4 I. Sobrados and M. Gregorkiewitz, *Phys. Chem. Miner.*, 1993, **20**, 433.

5 N. Petraanovic, V. Dondur and R. Dimitrijevic, *Mater. Sci. Monogr., (Ceram. Today—Tomorrow's Ceram., Pt. C)*, 1991, **66C**, 2229.

6 J. Berchot, D. Vivien, D. Gourier, J. Thery and R. Collongues, *J. Solid State Chem.*, 1980, **34**, 199.

7 J. B. Goodenough, H. Y.-P. Hong and J. A. Kafels, *Mater. Res. Bull.*, 1976, **11**, 203.

8 R. D. Shannon, *Phys. Chem. Miner.*, 1979, **4**, 139.

9 R. D. Shannon and T. Berzins, *Mater. Res. Bull.*, 1979, **14**, 361.

10 Y. Kubo, G. Yamaguchi and K. Kasahara, *Mineral. J.*, 1967, **5**, 213.

11 W. Schmitz, H. Siegel and R. Schoellner, *Cryst. Res. Technol.*, 1981, **16**, 385.

12 V. Dondur, V. Rakic, R. Dimitrijevic and D. Vucinic, *Thermochim. Acta*, 1985, **93**, 753.

13 M. Murat, *J. Therm. Anal.*, 1972, **4**, 73.

14 A. J. Perrotta and J. V. Smith, *Mineral. Mag.*, 1965, **35**, 588.

15 J. V. Smith and O. F. Tuttle, *Am. J. Sci.*, 1957, **255**, 282.

16 L. Keller and G. McCarthy, JCPDS International Centre for Diffraction Data, File no. 35–424.

17 H. G. F. von Winkler, *Acta Crystallogr.*, 1948, **1**, 27.

18 D. Müller, W. Gessner, H.-J. Behrens and G. Scheler, *Chem. Phys. Lett.*, 1981, **79**, 59.

19 E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak and G. Engelhardt, *J. Am. Chem. Soc.*, 1981, **103**, 4992.

20 J. M. Newsam, *J. Phys. Chem.*, 1985, **89**, 2002.

21 J. G. Thompson, R. L. Withers, A. K. Whittaker, R. M. Traill and J. D. Fitz Gerald, *J. Solid State Chem.*, 1993, **104**, 59.

22 M. Wark, W. Lutz, G. Shulz-Ekloff and A. Dyer, *Zeolites*, 1993, **13**, 658.

23 F. Helfferich, *Ion Exchange* McGraw-Hill, New York, 1962.

24 H. S. Sherry, *Molecular Sieve Zeolites—1, Adv. Chem. Ser.*, ACS, Washington, DC, 1971, vol. 101, p. 350.

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