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A new hydroxide-based synthesis method for inorganic polymers

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Abstract A new synthesis method is described to produce aluminosilicate inorganic polymers by direct reaction of aluminium hydroxide with amorphous silica under alkaline conditions. XRD and ^{27}Al and ^{29}Si MAS NMR spectroscopy suggest that the reaction mechanism involves the dissolution of the aluminium hydroxide in the alkali. The best results are obtained with more reactive gibbsite of small particle size and X-ray amorphous ρ-alumina containing 5-fold coordinated Al, and with compositions in the previously reported optimum range (SiO_2: Al_2O_3 = 3.0, M_2O: SiO_2 = 0.34, H_2O: M_2O = 9.4). Unreacted aluminium hydroxide occurs where there is insufficient silica for complete inorganic polymer formation but the reaction is less sensitive to variations in the K_2O: Al_2O_3 and K_2O: SiO_2 ratios. Zeolite formation was not observed in any of the present samples. More complex alumina sources such as thermally activated hydrotalcite can also be used to form an inorganic polymer, but under the alkaline synthesis conditions the unused alumina reacts with the poorly crystalline MgO present to re-form hydrotalcite, presumably containing atmospheric carbonate as the interlayer anion. This synthesis method can also potentially be extended to hydroxides other than those of aluminium.

Introduction

Inorganic polymers, also known as geopolymers, are X-ray amorphous materials, usually aluminosilicates, composed of a network of randomly arranged silicate and aluminate tetrahedra in conjunction with charge balancing alkali metal cations [1, 2]. Aluminosilicate geopolymers are conventionally synthesised at approximately ambient temperature by reaction of a solid aluminosilicate source, e.g. dehydroxylated kaolin clay (metakaolinite) with an alkali silicate solution under highly alkaline conditions [1, 2]. Industrial wastes such as fly ash or blast furnace slag have also been proposed as the solid reactants, especially for low-energy cement applications [3], but the resulting products are more properly described as alkali-activated cements.

Metakaolinite-based geopolymers are versatile materials with potential applications as ecologically friendly substitutes for Portland cement, fireproof materials, hazardous waste remediation [3], or more advanced applications as precursors for ceramic compounds [4], electronic materials [4], bioactive ceramics [5] or nanoporous materials for passive cooling of buildings [6]. The inorganic polymer systems for these applications can be characterised by their oxide composition, of which the optimal ratios for cured strength and viability are reported [2] to be of the order SiO_2: Al_2O_3 = 3.0–4.0, M_2O: SiO_2 = 0.25–0.45, H_2O: M_2O = 10–17.5.

In addition to the conventional synthesis method, two other synthesis methods for inorganic polymers have been proposed. One of these utilises a solid-state reaction between the undehydroxylated clay mineral and the appropriate alkali metal hydroxide, followed by hydration with a small amount of water which causes the material to set and harden at approximately ambient temperature [7]. This method can be modified by dry-mixing a

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pre-synthesised alkali metal silicate powder with metakaolinite, followed by the hydration step, and this variant has been used in the synthesis of lithium inorganic polymers [8].

In another synthetic approach, the use of a solid aluminosilicate as one of the reactants has been avoided altogether by reacting solutions of alkali aluminate with alkali silicate prepared in situ from alkali hydroxide and finely divided silica to form a material that cures and hardens at 40 °C to a solid with good compressive strength [9]. The advantage of this method is that it can be applied to inorganic polymers other than aluminosilicates, and has successfully been used to synthesise gallium silicate analogues with potentially interesting electronic properties [4].

In order to extend the range of inorganic polymers beyond the aluminosilicates, thereby opening up new applications, ever more versatile syntheses will be required that do not depend on the availability of solid reactants such as metakaolinite but which are similarly reactive and ubiquitous. The metal hydroxides constitute such a group that might potentially be used in conjunction with alkali silicate solutions to synthesise viable inorganic polymers. The present work tests this possibility by synthesising aluminosilicate inorganic polymers from solid aluminium hydroxides and related compounds by reaction with silica of fine particle size. The geopolymeric nature of the product was confirmed by XRD and ^{29}Si and ^{27}Al MAS NMR spectroscopy, and the possible use of the method for geopolymer synthesis from other starting materials was investigated.

Experimental

Aluminium hydroxide of fine particle size (Riedel-de-Haen) was used as the alumina source; this was shown by XRD to consist solely of gibbsite, $Al(OH)_3$, and its mean particle size, determined by a Malvern Mastersizer 2000 particle size analyser, was 14 µm. In other experiments, the synthesis method was tested using ρ-alumina (Alphabond 300, Almatis Gmbh, Germany) and synthetic hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (Kyowa Chemical Industry Company Ltd). XRD showed the ρ-alumina to be X-ray amorphous, and the hydrotalcite to be of good crystallinity, conforming to PDF no. 01-89-460. The latter was thermally activated at 400 °C before use, resulting in the loss of the crystalline hydrotalcite reflections and their replacement by two broad, diffuse features in the region of the major MgO reflections. The silica source in all the syntheses apart from the hydrotalcite polymers was Microsilica 600, a naturally occurring New Zealand fine amorphous silica with a mean particle size of 10 µm (Microsilica NZ). The hydrotalcite-based inorganic polymers were prepared from fine silica fume (Elkem ASA, Norway).

Table 1 Molar compositions of the samples

Sample	Alumina source	SiO_2: Al_2O_3	K_2O: Al_2O_3	K_2O: SiO_2	H_2O: K_2O
G1	$Al(OH)_3$	3.02	1.04	0.34	9.40
G2	$Al(OH)_3$	2.14	0.73	0.34	10.99
G3	$Al(OH)_3$	1.74	0.59	0.34	12.76
G4	$Al(OH)_3$	2.14	0.98	0.46	9.79
G5	$Al(OH)_3$	1.74	0.99	0.57	9.79
R	ρ-Al_2O_3	3.09	0.97	0.31	6.55
H	Hydrotalcite	3.15	2.02	0.67	9.40

The samples were synthesised by dry-mixing the solid silica and aluminium sources in a range of molar ratios shown in Table 1. The compositions based on gibbsite fall into two series, one (samples G1, G2 and G3) in which the K_2O: SiO_2 ratio was maintained constant, and the other (samples G1, G4 and G5) in which the K_2O: Al_2O_3 ratio was held approximately constant. Each of these series contained samples spanning a range of SiO_2: Al_2O_3 ratios up to about 3. An aqueous solution of potassium hydroxide (BDH reagent grade) was added to the dry mixtures and if required, the minimum quantity of extra water was added to achieve a workable paste. The composition of samples G1, R and H was close to the optimal molar ratio range [2], although sample R required less water and sample H required a higher K_2O: SiO_2 ratio to achieve a workable mixture.

The mixed pastes were placed in polythene moulds, vibrated to remove air bubbles, sealed with plastic film and cured at 40 °C for 3 days to form hard, durable monolithic samples. After drying at 40 °C the samples were powdered and examined by XRD (Philips PW1700 with computer-controlled goniometer and graphite monochromator using Cu Kα radiation) and ^{27}Al and ^{29}Si MAS NMR spectroscopy at 11.7T (Bruker Avance 500 spectrometer) under the following conditions:

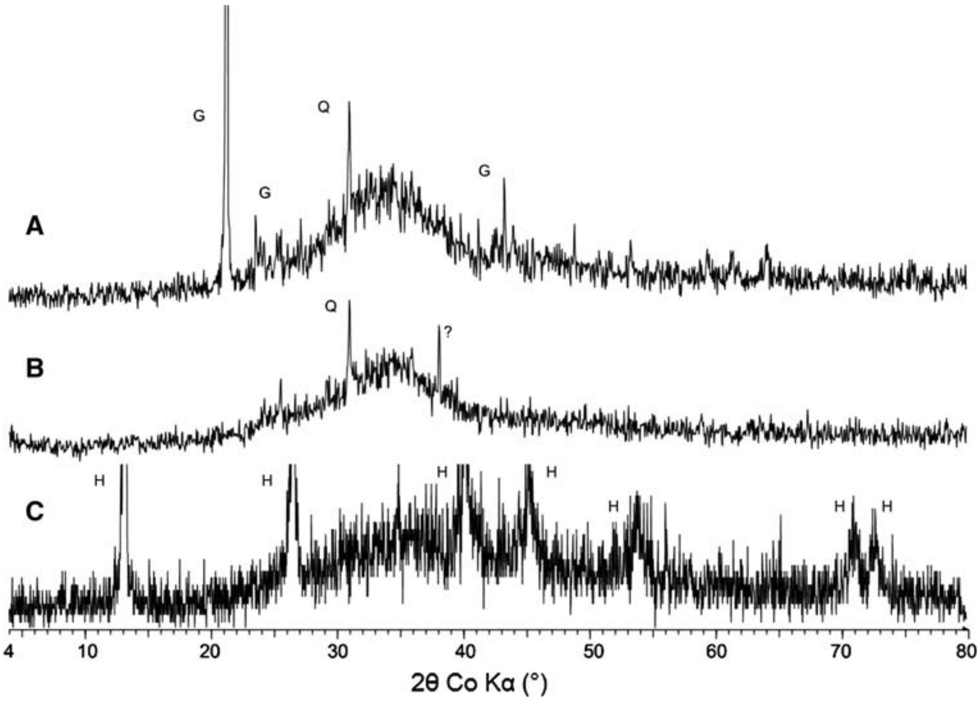
^{27}Al: 1 s (π/10 pulse for solution) with a 1 s delay, using a 4 mm Doty MAS probe spun at 10–12 kHz, the spectra referenced to $Al(H_2O)_6^{3+}$.

^{29}Si: 6 µs (π/10) pulse with a 30 s delay, using a 5 mm Doty MAS probe spun at 5–6 kHz, the spectra referenced to TMS.

Results

The samples of all the present compositions cured satisfactorily to form viable, hard monolithic materials. Representative XRD diffractograms of the synthesised materials are shown in Fig. 1. The gibbsite-based sample G1 closest to the optimum composition (Fig. 1A) contains the broad amorphous feature centred at about 30°2θ characteristic of an aluminosilicate inorganic polymer [2], with superimposed sharp reflections of unreacted crystalline gibbsite and a

Fig. 1 Representative XRD traces of inorganic polymers synthesised from (*A*) gibbsite, sample G1, (*B*) ρ-Al_2O_3, sample R, (*C*) thermally activated hydrotalcite, sample H. *Key*: *G* gibbsite (PDF no. 12-460), *Q* quartz (PDF no. 33-1161), *C* cristobalite (PDF no. 3-1425), *H* hydrotalcite (PDF no. 22-700)



trace of quartz, the latter originating as an impurity in the silica source. As the composition of the gibbsite-based samples is progressively shifted away from the optimum values, the reaction becomes less complete, as judged from the amount of unreacted gibbsite in the samples (estimated visually from the peak intensity of the major gibbsite reflection at $d = 4.86$ Å relative to that of the inorganic polymer feature). On this basis, the degree of reaction in the gibbsite-based samples was found to decrease as the SiO_2:Al_2O_3 ratio decreased below the optimum value of 3, but no zeolitic phases were found to form at the lowest SiO_2:Al_2O_3 ratios. By contrast, the reaction was found to be less sensitive to an effective decrease in the amount of alkali (as in samples G2 and G3) or an increase in the amount of alkali (as in samples G4 and G5).

The XRD diffractogram of the inorganic polymer prepared from ρ-alumina (Fig. 1B) shows a broad amorphous inorganic polymer feature with traces of cristobalite and quartz from the silica source, and a trace of an unidentified phase. The XRD trace of the sample H derived from hydrotalcite (Fig. 1C) shows the typical broad X-ray amorphous inorganic polymer signature, with the reappearance of the principal hydrotalcite reflections, albeit slightly more diffuse than in the original hydrotalcite. This suggests the dehydroxylated hydrotalcite has supplied some of its aluminium for the formation of an inorganic polymer, but under the alkaline synthesis conditions, the remaining alumina has reacted with the poorly crystalline MgO present to re-form hydrotalcite, presumably containing atmospheric carbonate as the interlayer anion.

Representative ^{27}Al NMR spectra of the samples are shown in Fig. 2. All the spectra contain two peaks, a characteristic inorganic polymer resonance at about 60–69 ppm corresponding to tetrahedrally coordinated aluminium [2], and an

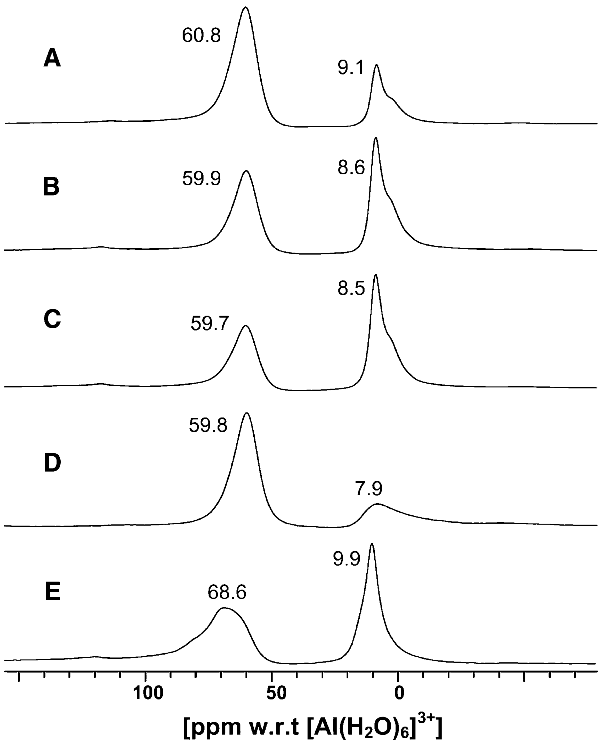


Fig. 2 Representative 11.7T ^{27}Al MAS NMR spectra of inorganic polymer samples synthesised from (*A*) gibbsite, sample G1, (*B*) ρ-Al_2O_3, sample R, (*C*) thermally activated hydrotalcite, sample H

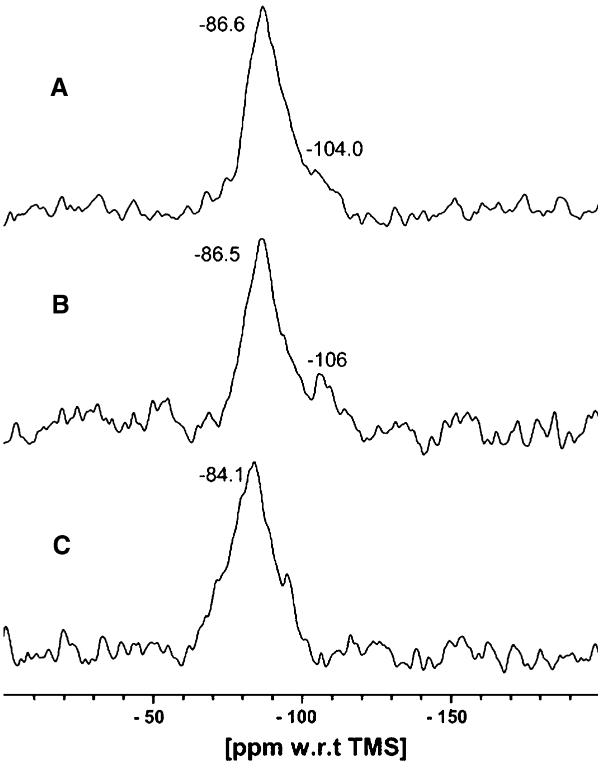


Fig. 3 Representative 11.7T ^{29}Si MAS NMR spectra of inorganic polymers synthesised from (*A*) gibbsite, sample G1, (*B*) ρ-Al_2O_3, sample R, (*C*) thermally activated hydrotalcite sample H

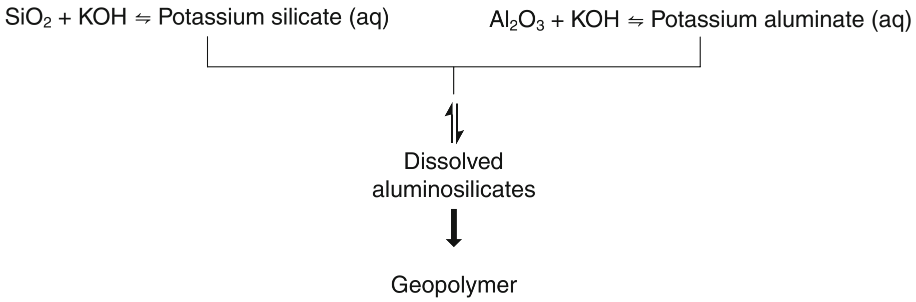
asymmetric peak at 8–10 ppm corresponding to unreacted octahedrally coordinated aluminium from the alumina source material. The octahedral resonance in the gibbsite-based samples (Fig. 2A–C) shows evidence of two overlapping octahedral species, the position of the sharper peak of the two corresponding to that of unreacted gibbsite [10]. The relative amount of unreacted aluminium in the gibbsite-based G series of samples, indicated by the relative NMR intensity of the octahedral resonance, followed the same trend as indicated by XRD. Sample G5 (not shown) contained an additional small peak at 80 ppm due to potassium aluminate in excess of that required to participate in the formation of the inorganic polymer. The spectrum of sample R (Fig. 2D) contains no trace of the resonance at about 30 ppm from the 5-fold coordinated Al in the original ρ-alumina [11], confirming that this starting material is highly reactive under the present conditions.

The spectrum of sample H (Fig. 2E) features a broad asymmetric tetrahedral peak at 68.6 ppm from unreacted dehydroxylated hydrotalcite and an octahedral peak at 9.9 ppm corresponding to hydrotalcite [12]. The size of the resonances suggests that in samples G1 and R the aluminium is predominantly located in an inorganic polymer, while in sample H some unreacted dehydroxylated hydrotalcite remains, and some hydrotalcite has reformed.

Typical ^{29}Si NMR spectra are shown in Fig. 3. Samples G1 and R (Fig. 3A, B) contain a principal resonance at about −86.5 ppm, typical of an inorganic polymer. Similar ^{29}Si spectra were observed for all the G-series of samples. In sample H (Fig. 3C) the major peak is shifted downfield to −84 ppm, reflecting the lower silicate connectivity resulting from the higher K_2O: SiO_2 ratio of this sample. Weaker signals at about −106 ppm due to free silica are present in the spectra of all the samples apart from those derived from hydrotalcite (Fig. 3C).

Discussion

The predominance of tetrahedral aluminium in sample G1 with component ratios close to the known range of optimal ratios demonstrates the viability of the method for producing geopolymers from gibbsite. Samples with component ratios significantly outside this range produced less well reacted materials when judged both on the basis of their content of unreacted gibbsite and their tetrahedral Al (although all the samples cured and set satisfactorily). This may be understood in terms of the various steps of the formation reaction of aluminosilicate inorganic polymers. It is known that this synthesis involves dissolved silicate and aluminate species [13]. At high pH values, both silica and aluminium hydroxide dissolve in potassium hydroxide to form potassium silicate and aluminate, respectively, which then react to yield dissolved aluminosilicate species. When the concentration of dissolved silica is in sufficient excess ($[SiO_2]$: $[Al_2O_3] > 2.5$), polymerisation occurs. In the present system this reaction can be summarised as:



Under the present reaction conditions and with the present reagents, sufficient dissolution of the solid alumina and silica reagents occurs to allow this reaction to proceed. As the SiO_2: Al_2O_3 ratio falls below the optimum value of 2.8–3, there is insufficient silica present to react with all the dissolved aluminate species, as reflected by the increase in the amount of unreacted alumina and the decrease in the relative amount of tetrahedral aluminium in the samples other than G1. The excess alumina remains as aluminium hydroxide, or if the reaction mixture is sufficiently alkaline, forms potassium aluminate. Interestingly, even at the lower SiO_2: Al_2O_3 ratios, no zeolitic phases are formed, by contrast with conventionally synthesised inorganic polymer systems in which zeolites are formed at low SiO_2: Al_2O_3 ratios [14].

The alkalinity of the system appears to be less significant, of secondary importance, since in sample G5, which has a very high alkali content, significant amounts of potassium aluminate are formed but are unable to react to form further inorganic polymer, as shown by the ^{27}Al NMR spectrum.

Thus, the present synthesis method is a viable alternative to other syntheses of aluminosilicate inorganic polymers, and has the potential to be extended to other aluminium sources, particularly to reactive forms such as ρ-alumina, and to mixed aluminium–magnesium reagents such as hydrotalcite. Even less-reactive alumina sources such as gibbsite of coarser particle size can be used as a starting material, although in that case the reaction is less complete (our unpublished results) suggesting that the reactivity of the alumina source is an important factor in the synthesis, and confirmed by the improved results achieved using more reactive aluminas such as ρ-alumina.

Conclusions

A new synthesis method has been developed to produce viable aluminosilicate inorganic polymers by direct reaction of amorphous silica with solid alumina sources such as aluminium hydroxide under alkaline conditions. Since the mechanism involves dissolution of the alumina source in the alkali, the most complete reaction is obtained with more reactive aluminas such as gibbsite of small particle size and ρ-alumina. Other alumina sources such as thermally activated hydrotalcite are also satisfactory starting materials for this synthesis, suggesting its applicability to a wider range of products.

A range of compositions is readily obtainable by altering the amounts of the starting materials, but the most complete formation of inorganic polymer occurs in mixtures within the previously reported range of optimum composition (SiO_2: $Al_2O_3 = 3.0$, M_2O: $SiO_2 = 0.34$, H_2O: $M_2O = 9.4$). As the starting composition deviates more widely from these optimum ratios, particularly the SiO_2: Al_2O_3 ratio, increasing amounts of unreacted aluminium hydroxide appear in the product in samples containing insufficient silica for complete inorganic polymer formation. The reaction is less sensitive to variations in the K_2O: Al_2O_3 and K_2O: SiO_2 ratios, although in samples of very high alkali content, a significant amount of potassium aluminate is formed, in excess of that required to participate in the formation of the inorganic polymer. Zeolite formation was not observed in any of the present samples.

Where a more complex alumina source such as thermally activated hydrotalcite is used, some of its aluminium is consumed in the formation of an inorganic polymer, but under the alkaline synthesis conditions, the remaining alumina reacts with the poorly crystalline MgO present to re-form hydrotalcite, presumably containing atmospheric carbonate as the interlayer anion.

Provided careful control is exercised over the SiO_2: Al_2O_3 ratio of the starting mixture, this synthesis method can produce aluminosilicate inorganic polymers from a variety of aluminium containing starting materials, and has the potential to be extended to hydroxides other than those to aluminium.

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