Characterization of chemosynthetic Al$_2$O$_3$–2SiO$_2$ geopolymers

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ABSTRACT

Pure chemosynthetic Al$_2$O$_3$–2SiO$_2$ geopolymers displaying positive alkali-activated polymerization properties and high compressive strength at room temperature were effectively fabricated utilizing a sol–gel method. The molecular structure of the precursor powder and resulting geopolymers were investigated by X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) analysis. In addition, the mechanical and alkali-activated polymerization properties of these materials were also studied. NMR data revealed that the chemosynthetic powders began to contain 5-coordinated Al atoms when the calcination temperatures exceeded 200 °C. These calcined powders were capable of reacting with sodium silicate solutions at calcination temperatures exceeding 300 °C, which is, however, much lower than the temperature required to convert kaolin to Metakaolin.

1. Introduction

Due to their sinter-free, easy fabrication and low cost, aluminosilicate geopolymers are rapidly finding their way into numerous industrial applications such as in solid electrolytes, the immobilization of toxic, hazardous and radioactive wastes, advanced structural tooling and refractory ceramics, fire resistant composites used in the construction of buildings, aircraft, ships, race cars, etc., as well as the nuclear power industry. Aluminosilicate geopolymers represent one class of cross-linked, long-chain inorganic polymers who's three-dimensional structure consists of tetrahedral [AlO$_4$] and [SiO$_4$] units, resulting in excellent physical properties, among which are high strength, anti-corrosion, resistance to heat and long life [1,2].

At present, raw materials such as Kaolin clays, Metakaolin, fly ash and blast furnace slag are often used to create aluminosilicate geopolymers. However, the chemical composition of these materials is very complicated and a fundamental investigation into the mechanism of geopolymerization has proven to be difficult. Although Metakaolin is usually used in the study of geopolymerization mechanisms because of its simple chemical composition compared to the other common precursor materials, impurities in the Metakaolin complicate the study of the geopolymerization process [3–6]. Usually, Metakaolin is fabricated through calcination of Kaolin (Al$_2$O$_3$·2SiO$_2$·2H$_2$O) at 600–900 °C [7,8], however, the Metakaolin is not pure and the atomic ratio of Al/Si is not consistent due to the fact that the age and location of the Kaolin mines are different.

In order to overcome these disadvantages, the present investigation focuses on preparing pure Si–Al materials which then can be alkali-activated to form geopolymers. In earlier works, Hos et al. [5] subjected alumina and silica to 1555 °C as thus prepared a melt-quenched material as a precursor for the production of a geopolymer. Brew and MacKenzie [6] synthesized geopolymers utilizing fumed silica, a solution of sodium hydroxide and sodium aluminate. The current study also employs pure sources of Si and Al for producing geopolymers. In this study, a sol–gel method was developed for synthesizing and purifying Al$_2$O$_3$–2SiO$_2$ powders from tetraethoxysilane (TEOS) and aluminum nitrate nine-hydrate (ANN) as the starting materials [9]. However, the preparation process and analysis of the results yield differences from that reported in previous work. Specifically, in this study, pure Al$_2$O$_3$–2SiO$_2$ powders were prepared by a sol–gel method and alkali-activation tests of the powders were carried out. Furthermore, the structural characteristics of the powders and geopolymers were determined by XRD and MAS NMR, and the mechanical properties were reported as well.

2. Experimental procedures

Starting materials for the sol–gel synthesis are tetraethylorthosilicate (TEOS) and aluminum nitrate nonahydrate (ANN). Solvents

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for the synthesis are anhydrous ethanol and distilled water. Starting materials and solvents were mixed in the following molar ratios: Al_2O_3–SiO_2 was 1:2 and SiO_2–H_2O to EtOH was 1:18:12. In a typical synthesis, two solutions were prepared while stirring: Solution A, TEOS was dissolved in EtOH; and solution B, ANN was dissolved in a mixture of EtOH and distilled water. Solution B was then added slowly to solution A while stirring, and the resulting mixture was maintained at 70 °C until a gel formed. The gel was then dried at 105 °C. Finally, the dried gel powders were calcined in air at temperatures of 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C, respectively, for 2 h.

The physical properties of the dried gel powders and the calcined powders were investigated as follows: the particle size of chemosynthetic Al_2O_3–$2SiO_2$ powder was investigated by Zetasizer Nano S laser diffraction particle size analyzer. Because the particle size distribution was a range but not a point, hence, it's difficult to assign any reason for the repetitiveness error of Zetasizer Nano S laser diffraction particle size analyzer. The surface area was investigated by SSA-3600 intelligent specific surface tester. The repetitiveness error of SSA-3600 intelligent specific surface tester was about ±2%. The dried gel powder and the calcined powder was respectively added into NaOH solution at pH 11 ± 0.2 the mass ratios: the powder to NaOH solution was 1:20. The mixed liquid was stirred for 4 h, then was centrifugated by H1650 high speed bench centrifugal machine for 30 min at the speed of rotation 8000 r min^{-1}, at last the Al dissolution of up layer clear solution was investigated by EDTA titrate. The repetitiveness error of EDTA titrate was about ±1%.

A solution of sodium silicate (modulus, 2.8) and solid sodium hydroxide was mixed while stirring to produce an activator solution (modulus, 1.2), which reacted with the dried gel powders and calcined powders, respectively. Additional distilled water was added to adjust the water content of the mixture (the mass ratio of calcined powders to the solution of sodium silicate (modulus, 1.2) was 1:1). The geopolymeric paste was cast into 2.0 cm × 2.0 cm × 2.0 cm cubic molds and cured at room temperature for 72 h. The cubes were then removed from the mold and tested for compression strength using a XWW-20CE Universal Tester, and the repetitiveness error of the XWW-20CE Universal Tester was ±5%.

X-ray diffraction was recorded on an automated D/Max B X-ray diffractometer using Ni-filtered Cu Kα radiation with a scanning rate of 0.5° per min from 10° to 65° (2θ). An acceleration voltage of 40 kV and a current of 10 mA were applied.

^{29}Si and ^{27}Al NMR spectra were obtained on a Bruker AV300 NMR spectrometer with a 4 mm probe spin at 8 kHz for Al and 5 kHz for Si. The NMR conditions for ^{27}Al were 78.2 MHz resonance frequency, a 0.55 µs pulse width, a 1 s delay, referred to $Al(H_2O)_6^{3+}$; and for ^{29}Si were 59.6 MHz resonance frequency, a 1.9 µs pulse width, a 15 s delay, referred to tetramethylsilane (TMS).

3. Results

In this experiment, nanometer gel particles with a D_{50} of approximately 80 nm were obtained by a sol–gel method, however, this was improved to approximately 250 nm following calcination at 800 °C for 2 h. Compared with natural Metakaolin, the layered structure of the Al_2O_3 and SiO_2 within the synthetic powder was clearly not the same as in the Metakaolin, even after acidic leaching (immerged in 10 M sulphuric acid for 10 h). The reason for this is that the alumina, but not the silica, dissolves in sulphuric acid. SEM images are shown in Fig. 1(a) and (b). The experimental results indicate that the synthetic Al_2O_3–$2SiO_2$ powders also have an irregular layered structure, which is different from that of natural Metakaolin, with an individual layer likely composed of many particle clusters, as shown in Fig. 1(b).
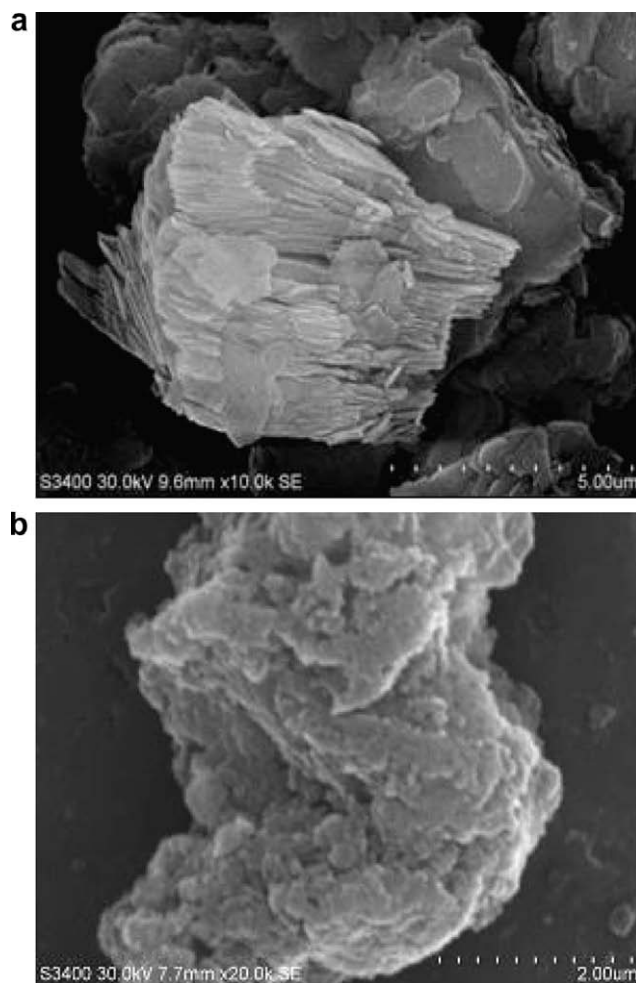

Fig. 1. SEM photo of erosional powders in 10 mol L^{-1} sulphuric acid for 10 h: (a) natural Metakaolin, and (b) synthetic Al_2O_3–$2SiO_2$ powder.

The results of the compressive strength of synthetic Al_2O_3–$2SiO_2$ geopolymers are presented in Table 1. These data indicate that the harden geopolymeric sample produced from powder calcined at 200 °C had no strength, while maximum strength was obtained when the precursor material was calcined at temperatures in the range of 700–800 °C. However, when calcination temperatures exceeded 800 °C, the compressive strength of the geopolymer was lost.

This effect of precursor calcination temperature on the strength of the geopolymer is similar to what is observed with Metakaolin [7,8]. A more detailed observation, however, reveals that calcined powders begin to manifest effects at 300 °C, while in the case of Metakaolin, the effects usually appear at about 500 °C. This observation suggests that Al_2O_3–$2SiO_2$ geopolymers produced from chemosynthetic Al_2O_3–$2SiO_2$ powders might possibly be prepared at lower temperatures than Metakaolin geopolymers. Such a lower temperature effect might allow for the addition of property-enhancing additives that otherwise would be unstable at the high temperatures required to prepare Metakaolin geopolymers.

Table 2 presents a comparison between the physical properties of the dried gel powders and the calcined powders. Clearly, the calcination process aggrandizes the surface area of synthetic Al_2O_3–$2SiO_2$ powders, however, the Al dissolution in NaOH at pH 11 ± 0.2 is slightly greater than for the dried gel powders, 8.66 ± 0.09% vs. 6.04 ± 0.06%, respectively. Based on the data in Table 1, the Al dissolution in NaOH does not represent geopolymerization activity.

Table 1
Compressive strength of the samples synthesized from dried gel powders or calcined powders.

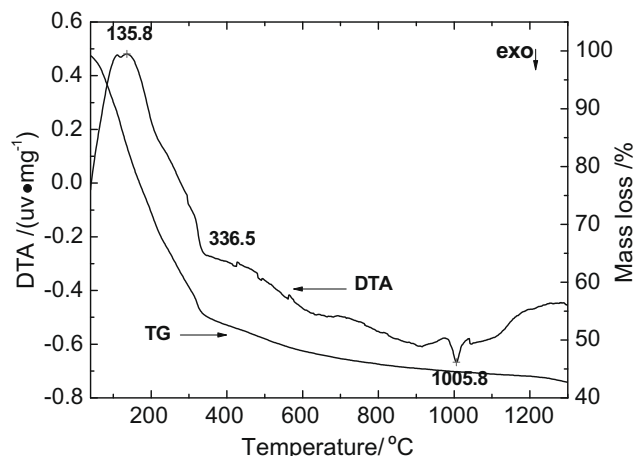| Starting material for samples	Dried gel powders	Calcined powders							
Calcined temperatures (°C)	105	200	300	400	500	600	700	800	900
Compressive strength of geopolymer material after casting for 72 h (MPa)	0	0	4.7 ± 0.2	4.8 ± 0.2	4.8 ± 0.2	14.2 ± 0.7	28.3 ± 1.4	28.2 ± 1.4	0

Table 2
Comparison of the physical properties between dried gel powders and calcined powders.

	Chemical composition (Si/Al)	Particle size D_{50} (nm)	Surface area (m^2/g)	Al dissolution in NaOH for 4 h (%)@pH 11 ± 0.2
Dried gel powders	1:1	50	669.27 ± 13.39	6.04 ± 0.06
Powders calcined at 800 °C for 2 h	1:1	250	321.58 ± 6.43	8.66 ± 0.09
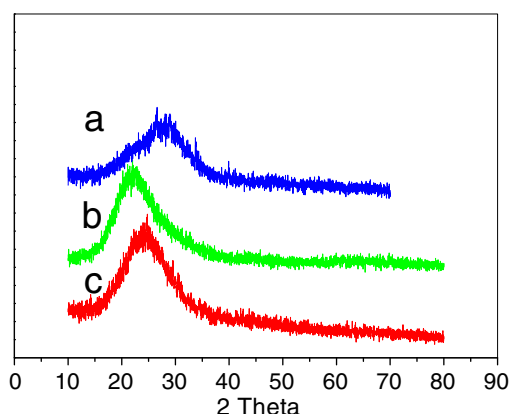
Fig. 2. XRD patterns of (a) geopolymeric material; (b) calcined powder at 800 °C for 2 h; and (c) dried gel powder at 105 °C.

Fig. 3. TG–DTA curves of the dried gel in air.

The XRD patterns of powders calcined at different temperatures are similar, with all samples showing a broad diffusion peak corresponding to a diffraction angle between 15° and 40°. The typical XRD patterns of Al_2O_3–$2SiO_2$ dried gels, calcined powders and geopolymeric materials are shown in Fig. 2. The center of the diffraction peak produced from the 800 °C-calcined powder is at lower angle than that of the dried gel. The size of the diffraction angle reflects the change in spacing between the aluminosilicate layers [5]. Thus, after calcination, the short range molecular structure of Al_2O_3–$2SiO_2$ should be more ordered than that in the non-calcined sample. The degree of polycondensation of the synthesized powders was verified by the reaction between calcined or dried gel Al_2O_3–$2SiO_2$ powders and $Na_2O·xSiO_2$ (x is 1.2 here) in aqueous solutions at room temperature. The experimental results indicate that dried gel powders lack polycondensation activity, while in contrast, the calcined powders exhibit good alkali polycondensation activity. Thus, geopolymers can be synthesized from calcined powders and aqueous alkali silicate at room temperature. Based on the experimental results, the inter-layer spacing of the aluminosilicate molecules may be the key factor in defining the microstructure, which can be characterized by solid state NMR.

Fig. 3 shows the TG–DTA curves of the dried gel in air. At a temperature of 1005.8 °C, an exothermic peak appeared on the DTA curve representing the formation of a crystalline phase. The analysis of that crystalline phase will be studied later.

4. Discussions

In this work, the compressive strength data have been collected from three samples at least. The compressive strength of geopolymer is some degree of uncertainty because of instrument factors and experimental samples, but we try to make the experimental errors to the lowest or smallest, such as measuring at the same time, many measuring samples, and so on. If the measuring errors are not over 10%, we think the changing tendency is to be trusted.

The ^{27}Al spectrum is generally considered the key factor in characterizing alkali-activated polymerization. Here, the ^{27}Al MAS NMR spectra of the dried gel and calcined powders are shown in Fig. 4. The spectrum of the dried gel consists of a single peak centered at approximately 1 ppm and assigned to 6-coordinated Al [Al(VI)], indicating that the Al environment of the dried gel is similar to that of kaolinite [8,9]. With increasing temperature, the calcined powders exhibit two new resonance peaks, one at approximately 55 ppm, attributable to 4-coordinated Al [Al(IV)] and one at approximately 25 ppm due to 5-coordinated Al [Al(V)]. The Al coordination changes of the powders are in agreement with those of dehydroxylated kaolinite [8,9]. In particular, it should be noted that the peaks related to Al(IV) and Al(V) appeared in the spectra of the powders calcined at 200 °C and 300 °C, while similar peaks usually appeared in kaolinite at temperatures over 480 °C. Rocha and Klinowski [10] believed that Al(V) was the principal indicator of the reactivity of the material and characterized a transitional state. The presence of Al(V) may explain why the dried gel calcined at 300 °C began to show some property of alkali-activation (see Table 1). In addition, the peaks attributed to Al(V) are strengthened as the temperature increases and this apparent increase in Al(V) corresponds to the increase in compressive strength, indicating that Al(V) may be directly involved (see Table 1 and Fig. 4), as originally suggested by Rocha and Klinowski [10].

The ^{29}Si spectra of the dried gel and calcined powders are shown in Fig. 5. The principal features of the ^{29}Si spectrum of the dried gel are the two peaks at approximately −103 ppm and −106 ppm, while the ^{29}Si spectrum of the calcined powder treated
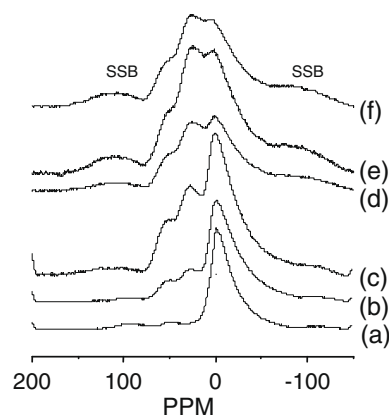
Fig. 4. ^{27}Al MAS NMR spectra of the dried gel at 105 °C (a) and powders calcined at various temperatures (SSB stands for spinning sidebands): (b) 200 °C; (c) 300 °C; (d) 600 °C; (e) 800 °C; and (f) 900 °C.
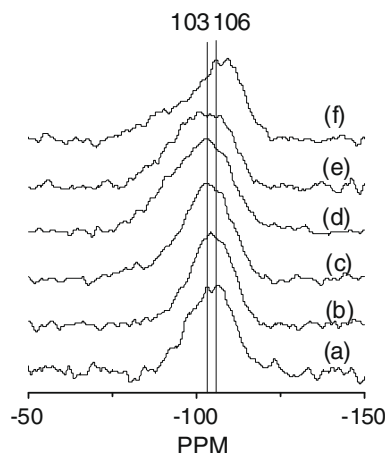

Fig. 6. ^{27}Al MAS NMR spectra of (a) the powder calcined at 800 °C and (b) its subsequent alkali-activated sample.

Fig. 5. ^{29}Si MAS NMR spectra of the dried gel at 105 °C (a) and powders calcined at various calcination temperatures: (b) 200 °C; (c) 300 °C; (d) 600 °C; (e) 800 °C; and (f) 900 °C.

at 200 °C contains a peak at approximately −104 ppm with two shoulders at around −103 ppm and −106 ppm. From the other ^{29}Si spectra shown in Fig. 5, we speculate that the peak at about −104 ppm for the calcined powders at 200 °C [spectrum (b)] may actually be an artifact resulting from the superposition of signals peaking at −103 and −106 ppm, which can be resolved in the other spectra. Framery and Mutin [11] have presented ^{29}Si MAS NMR spectra of an acid-catalyzed xerogel obtained from hydrolysis of tetraethoxysilane (TEOS) in ethanol without an Al source. Interestingly, the spectra indicated the presence of Q3 (−101 ppm) and Q4 (−110 ppm) sites in a ratio of roughly 1:1. Since the replacement of one silicon with one aluminum at a given site caused a downfield shift of approximately 5 ppm [14], the signal of −106 ppm in this study could be assigned to Q4 (1Al), while the signal at −103 ppm might be attributed to Q3, since the resonance peak of Si in Metakaolin is about −103 ppm [12,13]. Therefore, we see that data from XRD and ^{27}Al MAS NMR analysis all contain evidence of structural similarities between the powders calcined at 300–800 °C and Metakaolin.

Fig. 5 also indicates that the FWHMs (full-width-at-half-maximum) of the spectra of the powders calcined at 200 °C and 300 °C are approximately the same, about 16 ppm, which is far greater than that of kaolinite (about 2.5 ppm), and yet slightly less than that of Metakaolin (about 20 ppm) [8,9]. Therefore, these
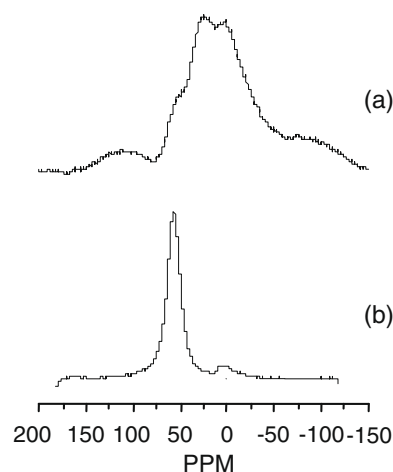
calcined powders possessed many of the characteristics of Metakaolin, such as an amorphous XRD pattern, the presence of Al(V) in Al NMR spectra, and the location and FWHMs of Si NMR spectra. In the study presented here, 200 °C-calcined powder was also amorphous, contained some Al(V), and began to display properties of alkali-activation in sodium silicate solutions. However, it demonstrated no compressive strength whatsoever, and therefore needs to be studied further.

With an increase in calcination temperatures up to 600 °C, the ^{29}Si spectrum of the samples still displays a peak at approximately −103 ppm and a shoulder at about −106 ppm. In addition, the center of gravity of the signal shifted downfield and the FWHM moved from about 16 ppm to 22 ppm. At 800 °C, the center of gravity of the signal remained shifted downfield, and a new peak appeared at approximately −101 ppm, possibly due to Q4 (2Al). With a change in temperature from 800 °C to 900 °C, the center of gravity of the spectrum shifted back to the higher magnetic field, with a peak at about −106 ppm and another peak at around −109 ppm, assigned to Q4 (0Al) and related to the presence of amorphous SiO_2 or cristobalite [8,9]. Since the maximum of each of the two peaks is nearly the same, it is possible they represent a single peak and if so the FWHM of the spectrum would be approximately 16 ppm (less than that at 800 °C). While the rationale presented here is not definitive, there is evidence that the environment of the Si atoms changes to a more ordered state (the formation of some crystalline phases) when the calcination temperature was shifted from 800 °C to 900 °C. Similar results appeared when kaolinite was calcined at about 850–900 °C [8,9]. Maybe this formation of some crystalline phases resulted in the powders not to display the alkali-activation property when treated above 900 °C.

The ^{27}Al MAS NMR spectra of the powder calcined at 800 °C and the subsequent alkali-activated sample are presented in Fig. 6. It appears that during the reaction, Al(V) and Al(VI) were converted to tetrahedral Al(IV) sites and as a result the broad spectrum was sharpened into a well-defined peak, which is a typical characteristic of geopolymers [12].

The ^{29}Si MAS NMR spectra of the powder calcined at 800 °C and its alkali-activated sample are presented in Fig. 7. The center of gravity of the signal was at about −102 ppm before the reaction, and then shifted to the typical geopolymer position of −92 ppm following the reaction. Previous studies show that ^{29}Si MAS NMR spectrum of fully cured geopolymers reveals a broad resonance peak located at approximatley −85 to −95 ppm depending on the Si/Al ratio [12,14,15]. In summary, the change in the ^{29}Si MAS NMR spectra of samples before and after the reaction also
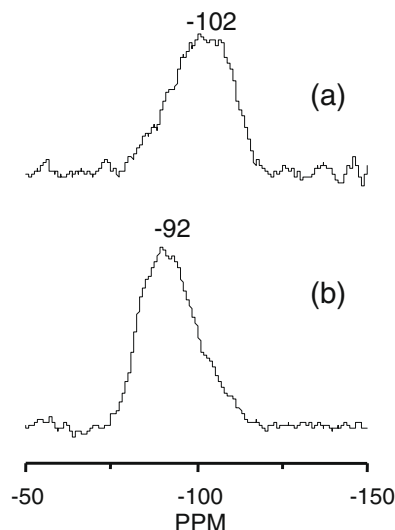
Fig. 7. ^{29}Si MAS NMR spectra of (a) the powder calcined at 800 °C and (b) its subsequent alkali-activated sample.

demonstrates the characteristics of geopolymerization, and in fact the spectra are similar to those of Metakaolin and its alkali-activated product.

Pure Al_2O_3–$2SiO_2$ precursors (powders) for a geopolymeric material have been prepared by a simple sol–gel method. The alkali-activated products derived from these precursors meet the general criteria for a geopolymer. Since the purity and Si/Al ratio of the precursors for the geopolymer are easily adjusted in the sol–gel process, the properties and composition of the precursors can be controlled with relative ease. Hence, these precursors and the geopolymers resulting from them need to be investigated further in order to fully understand their wide ranging potential applications.

5. Conclusions

Pure chemosynthetic Al_2O_3–$2SiO_2$ geopolymers displaying positive alkali-activated polymerization properties and high compressive strength at room temperature were effectively fabricated utilizing a sol–gel method. The molecular structure of the precursor powder and resulting geopolymers were investigated by X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) analysis. In addition, the mechanical and alkali-activated polymerization properties of these materials were also studied.

The results indicate that the reactivity of the chemosynthetic Al_2O_3–$2SiO_2$ powder was best when calcinated at temperatures from 300 °C to 800 °C, with the highest reactivity occurring in the powder calcined at 800 °C. For powder calcined below 300 °C or above 800 °C, no reactivity was observed due to the disappearance of Al(V). Therefore, the Al(V) might be directly involved in compressive strength as compressive strength was zero for precursors calcined below 300 °C or above 800 °C.

From NMR and XRD analyses, it can be shown that the microstructure of powders calcined at 300–500 °C is different from that of Metakaolin. For example, the powders start to become alkali-activated at a calcination temperature of 300 °C which is far lower than the temperature at which kaolin begins the transformation to Metakaolin.

Acknowledgments

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