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Preparation of geopolymer precursors by sol–gel method and their characterization

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Abstract Pure Al_2O_3–$2SiO_2$ precursors (powders) for a geopolymer were prepared by a sol–gel method. The alkali-activated products derived from the precursors meet the general criteria for a geopolymer. The structure of the powders was investigated by NMR, XRD, and FTIR analysis, and their alkali-activation properties were studied. The data show that the powders when heat treated at 200 °C begin to contain 5-coordinated Al, those heat treated at 300 °C can begin to undergo alkali-activation, and those heat treated at 300–800 °C possess a number of structure characteristics similar to metakaolin, and the properties of their alkali-activated products are similar to those of the metakaolin geopolymers.

Introduction

A geopolymer, first defined by Davidovits [1], should more appropriately be referred to as a type of “inorganic polymer” [2]. More specifically, a geopolymer is a three-dimensional aluminosilicate mineral polymer that contains a variety of amorphous to semicrystalline phases. The material exhibits excellent physical and chemical properties, such as high compressive strength, low shrinkage, fast or slow setting times, which are useful in a diverse range of potential applications, including immobilization of toxic, hazardous, and radioactive wastes, advanced structural tooling, and refractory ceramics [1, 3–5].

At present, materials such as metakaolin, fly ashes, and blast furnace slag are often used to produce geopolymers. However, since the chemical composition of these materials is very complex, a fundamental investigation of geopolymerization mechanism has proved to be difficult. Metakaolin is usually used in the study of geopolymerization mechanism, since its chemical composition is simple, compared to the other common precursor materials. However, impurities in metakaolin complicate the geopolymerization process [6, 7].

In order to overcome these disadvantages, the present investigation was aimed at preparing pure Si–Al–O materials, which can be alkali-activated to form geopolymers. In earlier work, Hos et al. [8] prepared a melt-quenched material as a precursor for the production of a geopolymer by using alumina and silica as starting materials at 1555 °C. Brew and MacKenzie [9] synthesized geopolymers using silica fume, sodium hydroxide solution and sodium aluminate. Gordon et al. [10] prepared “synthetic metakaolin” (SynMK) by an organic, steric entrapment method and synthesized geopolymers with it. This study also uses pure Si and Al sources for producing geopolymers. However, the preparation process and results of this investigation are different from those in a previous study. Specifically, in this study, pure Al_2O_3–$2SiO_2$ powders were prepared by sol–gel method, and alkali-activation tests of the powders were carried out. Further, the structural characterization of the powders by FTIR, XRD, and MAS NMR are reported. Although we published a paper [11] in which pure Si–Al–O precursors for geopolymers were prepared by sol–gel method, it mainly focuses on study on electrical conductivity of geoploymer materials.

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Experimental

Starting materials for the sol–gel syntheses were tetraethylorthosilicate (TEOS) and aluminium nitrate nonahydrate (ANN). Solvents for the syntheses were anhydrous ethanol and distilled water. Starting materials and solvents were mixed in the following ratio: the molar ratio of Al_2O_3 to SiO_2 was 1:2 and the molar ratio of SiO_2 to 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 maintained at 70 °C until a gel was formed. The gel was then dried at 105 °C. Then, the dried product (DP) was heat treated in air at different temperatures, respectively, for 2 h to make the heat-treated powders (HPs). Finally, The DP and HPs were milled and sieved through a 75-μm mesh sieve.

The activator solution (sodium silicate, modulus 1.2, solids content 42.7%) was reacted with the DP and HPs. The molar ratio is: $Al_2O_3/Na_2O = 1.0$, $H_2O/Na_2O = 10$ and $SiO_2/Al_2O_3 = 3.2$. The resulting resin was cast into unsealed 2.0 × 2.0 × 2.0 cm cubic moulds and cured at about 28 °C for 72 h. The cubes were then removed from the mould and tested for compressive strengths using universal tester.

Infrared spectra of the powders were recorded on a NiColet-5DX-FT spectrometer using the KBr pellet technique.

X-ray powder 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 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 spun 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).

Results and discussion

The effects of heat-treated temperatures of the precursors on compressive strengths

The results of the compressive tests are shown in Fig. 1.

These data show that there is no strength developed by the product at 200 °C and below. A modest temperature-related strength development is observed in the range of 300–500 °C. Between 600 and 800 °C, the strength rises to a maximum. At 900 °C, the strength is totally lost.

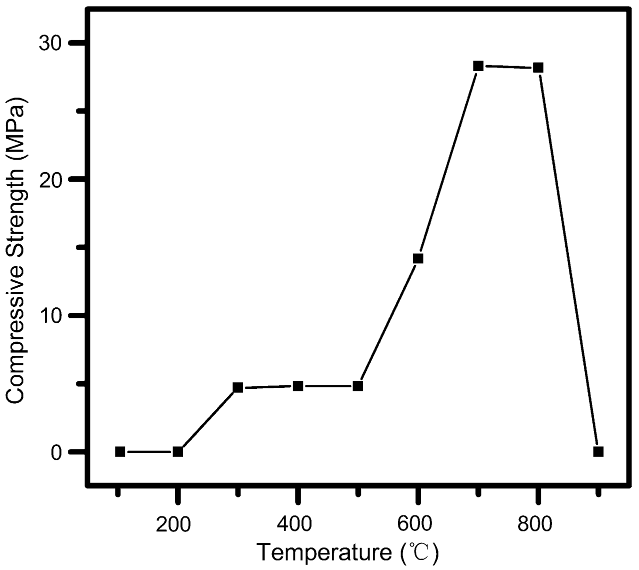

Fig. 1 Compressive strengths of the samples synthesized with DP (105 °C) and HPs (200–900 °C) at different heat-treated temperatures, respectively (Three replicates of each sample were used in the strength tests and each relative error was less than 8%)

For kaolin, the calcination temperature producing the reactive state is usually in the range of 600–800 °C [12]. Therefore, this temperature trend is similar to what is observed with metakaolin. A more detailed examination, however, shows that HP began to show effects at 300 °C, while kaolin usually begins to transform to metakaolin at about 500 °C. This result suggests that HP for manufacturing geopolymers might be made at lower temperatures than those used to produce metakaolin.

It should be noted that the cubes formed with the HPs that were prepared at 300–800 °C appeared white, smooth, fine, and similar to ceramic material. In addition, the cubes did not fragment when they were immersed in distilled water for 7 days at room temperature. This result suggests that the compressive strengths of the cubes are not due solely to the drying of excess sodium silicate between the particles.

FTIR analysis

The FTIR spectra of the DP and various HPs and an alkali-activated sample of the HP heat treated at 800 °C are shown in Fig. 2. The absorption peaks at about 3440 cm^{-1} and 1638 cm^{-1} are the stretching and bending vibration frequencies of the hydroxyl groups, respectively. The absorption peak at about 2350 cm^{-1} is due to adsorptive CO_2 vibration. Spectra (a) and (b) are quite similar. The

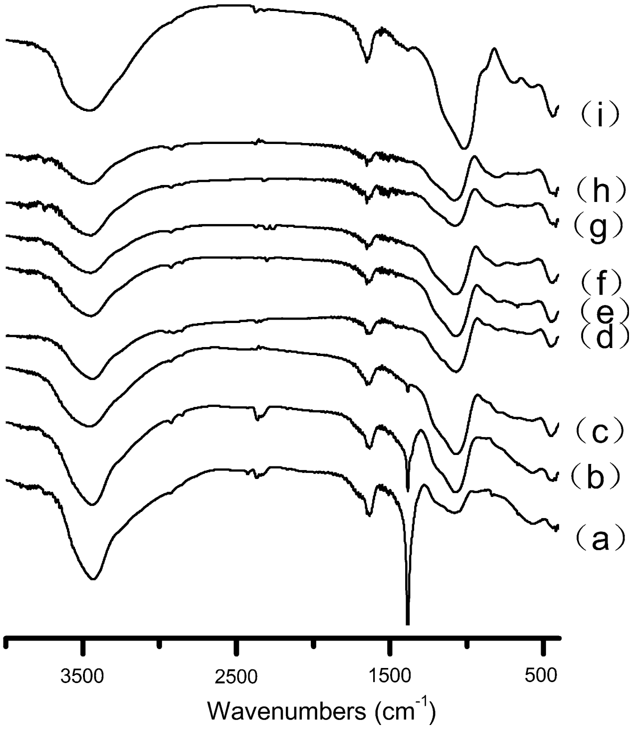

Fig. 2 FTIR spectra of the DP and HP at different heat-treated temperatures and alkali-activated sample: (a) DP at 105 °C; (b–h) HPs heat treated from 200 to 800 °C at increments of 100 °C; and (i) alkali-activated sample of HP at 800 °C heat-treated temperature

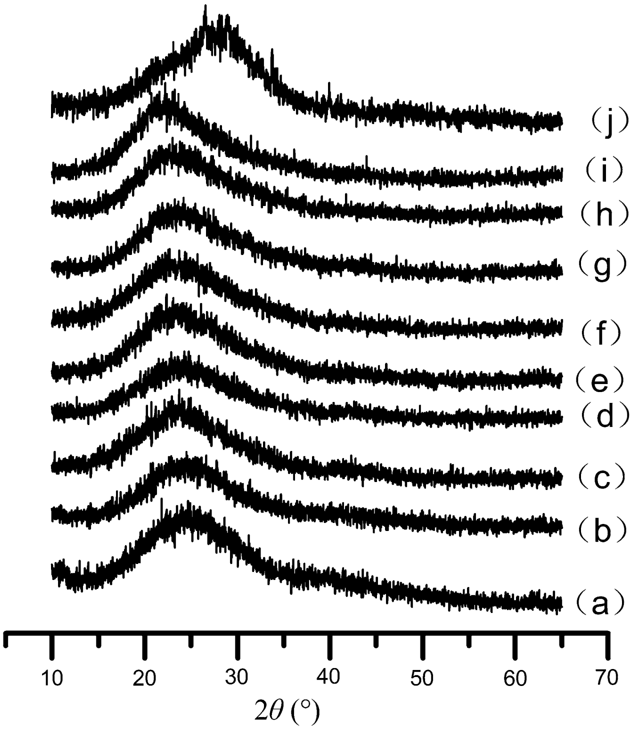

Fig. 3 XRD patterns of the DP and HP at different heat-treated temperatures and alkali-activated sample: (a) DP at 105 °C; (b–i) HPs heat treated from 200 to 900 °C at increments of 100 °C; and (j) alkali-activated sample of HP at 800 °C heat-treated temperature

absorption peak at about 1380 cm^{-1} in these two spectra is attributed to NO_3^- vibration [13], indicating that there is NO_3^- in both the DP and the HP heat treated at 200 °C. Spectra (c)–(h) are similar, except that there is a small absorption peak at 1380 cm^{-1} in spectrum (c), which shows that there is only a small amount of NO_3^- in the HP heat treated at 300 °C and none in the HPs heat treated at higher temperatures. The peaks at 1080, 810, and 460 cm^{-1} are consistent with the characteristic absorption peaks of metakaolin [14, 15]. This implies that the HPs heat treated at 300–800 °C possess structure characteristics similar to metakaolin. However, it needs be explained that metakaolin is a layered structure but HPs are not. The lack of structure in the rest of spectra suggests the general amorphous character of the powders.

The spectra of HP heat treated at 800 °C and its alkali-activated sample [(h) and (i) in Fig. 2] show the formation of typical geopolymer during reaction [14, 15]. The Si–O stretching absorption at 1080 cm^{-1}, shifts to lower wavenumber. The absorption at 810 cm^{-1} disappears, while a peak around 580 cm^{-1} and one around 700 cm^{-1} are formed. The change of the spectra of the HP before and after the alkali activation is similar to that of metakaolin and its alkali-activated product [14, 15].

XRD analysis

Figure 3 shows the XRD patterns of DP, the HPs, and an alkali-activated sample of the HP heat treated at 800 °C. The XRD pattern of DP and the HPs are quite similar, with an amorphous peak in the region of 22–24° (2θ) that is consistent with the typical amorphous peak seen in metakaolin [16–18]. These results reinforce the conclusion drawn from the FTIR study; that is, the structure of the HPs heat treated at 300–800 °C is generally amorphous and the HPs heat treated at 300–800 °C possess structure characteristics similar to metakaolin. The XRD pattern of alkali-activated sample of HP heat treated at 800 °C [(j)] reflects its amorphous character, with a peak (at $2\theta = 28°$) and a shape that is typical of geopolymers [17, 18].

NMR spectra

The ^{27}Al MAS NMR spectra of the DP, HPs, and an alkali-activated sample of the HP heat treated at 800 °C are shown in Fig. 4. The spectrum of the DP consists of only a single signal centered at about 1 ppm, assigned to 6-coordinated Al [Al(VI)]. With the rise of heat-treatment temperature, the HPs exhibit two new resonances at about

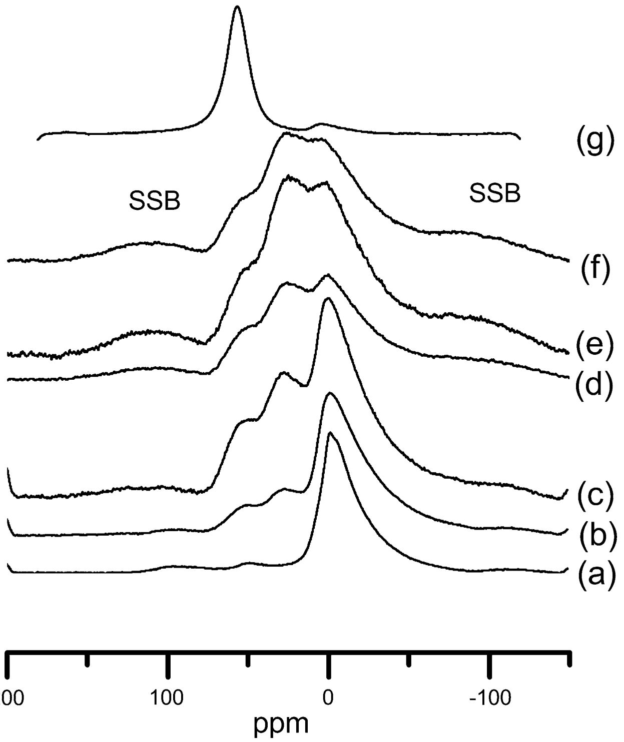

Fig. 4 ^{27}Al MAS NMR spectra of the DP, HP at different heat-treated temperatures and alkali-activated sample: (a) DP at 105 °C; (b) HP at 200 °C; (c) HP at 300 °C; (d) HP at 600 °C; (e) HP at 800 °C; (f) HP at 900 °C; and (g) alkali-activated sample of HP at 800 °C heat-treated temperature (SSB stands for spinning sidebands)

55 ppm, attributed to 4-coordinated Al [Al(IV)] and at about 25 ppm, due to 5-coordinated Al [Al(V)]. The Al coordination changes of the powders are in agreement with those of dehydroxylated kaolinite [19, 20]. In particular, it should be noted that the peaks related to Al(IV) and Al(V) appear in the spectrum of the 200 °C and 300 °C HP, while similar peaks usually appear in kaolinite at temperatures over 480 °C. Rocha and Klinowski [21] believe that Al(V) is the principal indicator of the reactivity of material, and characterizes a transitional state. The presence of Al(V) may explain why HP heat treated at 300 °C begins to show some alkali-activation properties (see Fig. 1). In addition, the peaks attributed to Al(V) are strengthened with the rise of temperature. This apparent increase in Al(V) corresponds with the increase in compressive strengths, which suggests Al(V) may be directly involved with increased compressive strengths (see Figs. 1 and 4), as originally suggested by Rocha and Klinowski.

The ^{27}Al spectra of 800 °C-heat treated HP and its alkali-activated sample [(e) and (g) in Fig. 4] show the occurrence of geopolymerization. During the reaction, Al(V) and Al(VI) are converted to tetrahedral sites of Al(IV) and the broad spectrum is sharpened into a well-defined peak, which is characteristic of geopolymers [2, 22].

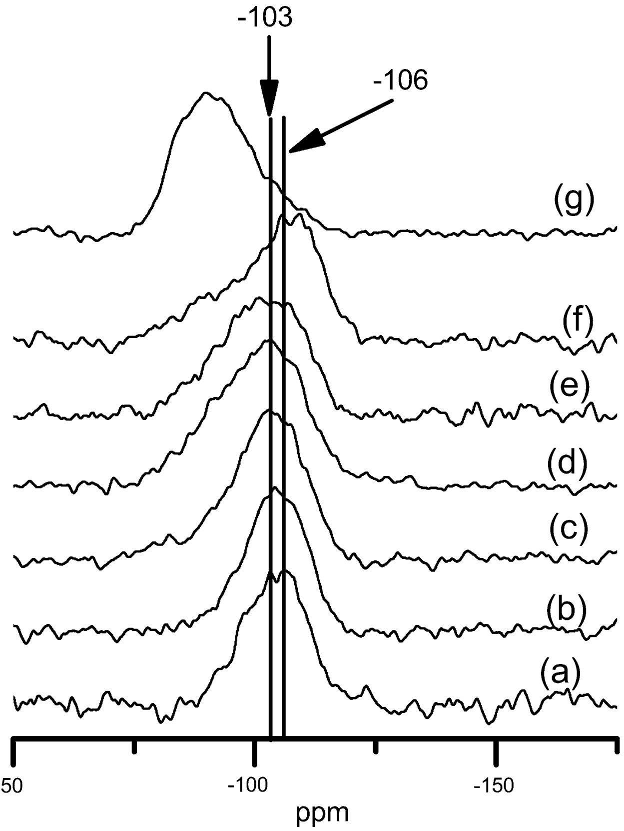

Fig. 5 ^{29}Si MAS NMR spectra of the DP, HP at different heat-treated temperatures and alkali-activated sample: (a) DP at 105 °C; (b) HP at 200 °C; (c) HP at 300 °C; (d) HP at 600 °C; (e) HP at 800 °C; (f) HP at 900 °C; and (g) alkali-activated sample of HP at 800 °C heat-treated temperature

The ^{29}Si MAS NMR spectra of the DP, HPs, and an alkali-activated sample of the HP heat treated at 800 °C are shown in Fig. 5. The principal features of the ^{29}Si spectrum of the DP seem to be two peaks at about −103 and −106 ppm. However, it is more likely for the spectral feature to be a broad peak considering that the noise level in the background. The center of gravity of the spectrum is at about −104.5 ppm. Framery [23] has presented ^{29}Si MAS NMR spectra of the acid-catalyzed xerogel obtained from hydrolysis of tetraethoxysilane (TEOS) in ethanol without Al source. In particular, the spectra indicate the presence of Q^3 (−101 ppm) and Q^4 (−110 ppm) sites in a ratio of roughly 1:1. In addition, the replacement of one silicon with one aluminum at a given site causes a downfield shift of about 5 ppm [24]; therefore, this signal may be assigned to mixtures of $Q^4(n\text{Al})$ and $Q^3(n\text{Al})$ sites.

With the increase of temperature, the center of gravity of the signal shifted to downfield at first. It should be noted that the change is small from 300 to 800 °C and the center is near −103 ppm, which is consistent with the peak of resonance of Si in metakaolin [22, 25]. However, with the change of temperature from 800 to 900 °C, the center of gravity of the spectrum shifts back to the higher magnetic field, with a peak at about −106 ppm and a peak at about −109 ppm, assigned to Q^4(0Al) and related to the presence of amorphous SiO_2 or cristobalite [19, 20, 26, 27]. This means that the environment of Si atoms has been changed, and there may be the formation of some crystalline phases when treatment temperature is shifted from 800 to 900 °C. Similar results appeared when kaolinite was heat treated at about 950–1000 °C [19] and 850–900 °C [20]. According to the analysis in Refs. [19] and [20], we suggest that the crystalline phases consist of some cristobalite germs. Maybe this change of the environment of Si atoms results in the powders not to display the alkali-activation property when heat treated at 900 °C (see Fig. 1).

The ^{29}Si MAS NMR spectra of the 800 °C heat treated HP and its alkali-activated product [(e) and (g) in Fig. 5] also show the occurrence of geopolymerization. The center of gravity of the signal before the reaction is at about −103 ppm, while that after the reaction has shifted to about −92 ppm, positioned in the range of geopolymer resonance. From earlier work, it is known that ^{29}Si MAS NMR spectroscopy of fully cured geopolymers reveals a broad resonance location ranging from −85 to −95 ppm depending on the Si/Al ratio [22, 28].

In summary, HPs heat treated at 300–800 °C show some characteristics of metakaolin, such as amorphous XRD pattern, the evolution of Al(V) in Al NMR spectra, and the site of Si NMR spectra, and similar wave numbers and broadness of the absorption peaks in FTIR, and alkali-activation property, in spite of some differences. It should be noted that whether or not HP heat treated at 200 °C shows alkali-activation property in other conditions needs to be studied further. If process parameters are further investigated, HP heat treated at 200 °C may show alkali-activation properties, since the powders are also amorphous and contain some Al(V). Although we cannot draw a conclusion that the structure of the as-prepared powders is similar to that of metakaolin because metakaolin is in fact a layered structure and it is unlikely to be replicated in any sol–gel process, it is interesting to note that they possess a few structure characteristics similar to metakaolin by NMR, XRD, and FTIR analysis and can be alkali activated.

Conclusions

The pure Al_2O_3–$2SiO_2$ precursors (powders) for a geopolymer have been prepared simply by a sol–gel method. The alkali-activated products derived from the precursors meet the general criteria for a geopolymer [9, 29–31]. 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, the uses of the precursors and their associated geopolymers should be investigated more fully to explore newer and wider range of applications for these materials.

By NMR, XRD, and FTIR analysis, we have generated evidence that HPs heat treated at 300–800 °C possess a number of structure characteristics similar to metakaolin. Future study of the geopolymerization reaction mechanism is likely to be simplified using the HPs as starting materials since there are no other metal ions to complicate the geopolymerization reaction as there are in the natural material.

The heat-treated temperature at which the powders begin to get alkali activated is lower than that at which kaolin begins to transform to metakaolin. Further study of this phenomenon will provide additional insights to the geopolymerization reaction.

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