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Characterization of chemosynthetic Al_2O_3–$2SiO_2$ geopolymers

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ABSTRACT

Pure chemosynthetic Al_2O_3–$2SiO_2$ geoploymers 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 ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) 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_2O_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_2O_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 $2.0\ cm \times 2.0\ cm \times 2.0\ cm$ 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).

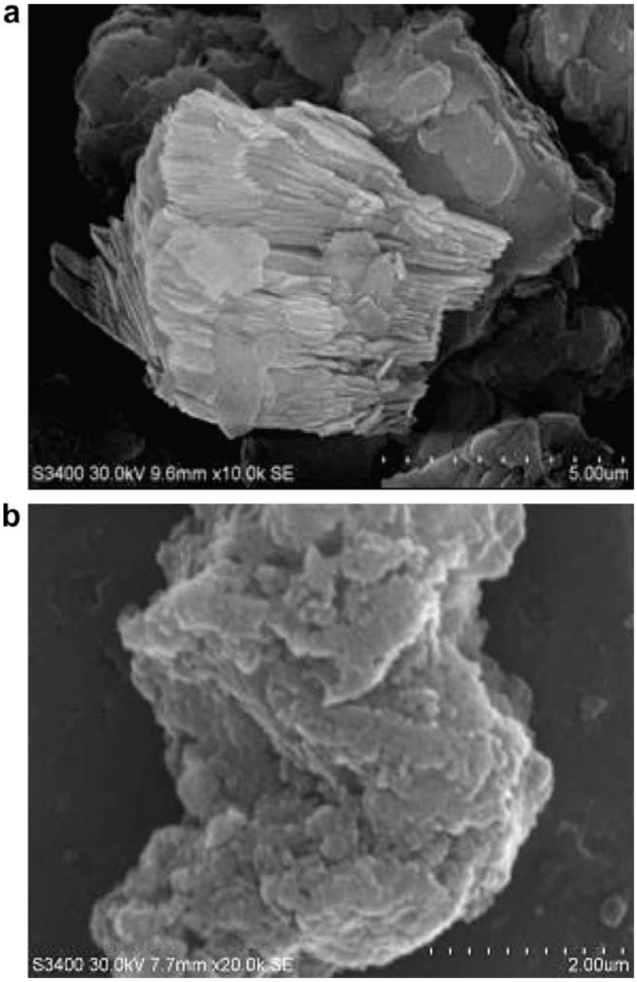

Fig. 1. SEM photo of erosional powders in 10 mol L^{-1} sulphuric acid for 10 h: (a) natural Metakaolin, and (b) synthetic Al_2O_3–$2SiO_2$ powder.

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, $8.66 \pm 0.09\%$ vs. $6.04 \pm 0.06\%$, respectively. Based on the data in Table 1, the Al dissolution in NaOH does not represent geopolymerization activity.