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Preparation of nano-sized Al_2O_3–$2SiO_2$ powder by sol–gel plus azeotropic distillation method

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ABSTRACT

Nano-sized amorphous Al_2O_3–$2SiO_2$ powder was prepared by a sol–gel method coupled with azeotropic distillation. The structure of the powder was investigated by DTS, BET, TEM, FT-IR, TG-DTA and XRD, showing that *n*-butanol azeotropic distillation could effectively remove water from the aluminosilicate gels and prevent the formation of hard agglomerates in the drying process. The average particle diameter of the powder was about 70 nm. The largest BET specific surface area of the powder was 669 m^2/g. To examine the alkali-activation reactivity of the powder, alkali-activation tests were performed with the powder reacting with sodium silicate solution. The synthetic powder was found to be highly reactive.

1. Introduction

Inorganic geopolymers have attracted considerable attention as novel materials. Similar to natural zeolite minerals, geopolymers, a class of aluminosilicate materials with three-dimensional network first developed by Joseph Davidovits (1988a), exhibit excellent physical and chemical properties, such as high compressive strength, low shrinkage, fast or slow setting time, making them useful in a diverse range of potential applications, including immobilisation of toxic, hazardous and radioactive wastes, and advanced structural tooling and refractory ceramics (Davidovits, 1988a, 1988b, 1991; van Jaarsveld, van Deventer, & Lorenzen, 1997).

Raw materials for producing geopolymers can be industrial wastes, such as fly ash and blast furnace slag, or such natural minerals as kaolin and albite. Metakaolin (MK), a product of calcining kaolin at 600–900 °C in air, is a good raw material for making high-strength geopolymers, which are often utilized in building materials and fire-resistant materials. Since chemical composition of metakaolin is simple, compared to certain other raw materials, we prepared pure Al_2O_3–$2SiO_2$ powder by a sol–gel method, referring to principal chemical composition of metakaolin (Zheng, Cui, Zhang, & Tong, 2009a, 2009b). We believe the preparation of pure Al_2O_3–$2SiO_2$ powder for making geopolymers would benefit the investigation on geopolymerization. Considering that nano-sized powder may be different from micro-sized powder in certain performances, we set out to search for a method of synthesizing nano-sized Al_2O_3–$2SiO_2$ powder. It is very important to prevent or suppress the formation of hard agglomerates while preparing nano-sized powder using the sol–gel method. Two effective methods are usually available: supercritical drying and freeze-drying, by which hard agglomerate formation could be avoided (Litchfield & Liaips, 1979; Luan, Gao, & Guo, 1998; Tewari, Hunt, & Lofftus, 1985). However, both supercritical drying or freeze-drying called for high-temperature and/or high-pressure operation. Although under normal atmospheric temperature and pressure, washing gel by organic solvent could reduce the formation of hard agglomerates, large quantities of organic solvent would be consumed and water molecule could not be effectively removed (Zhang & Hu, 1996) to prevent hard agglomerate formation. Azeotropic distillation, using *n*-butanol as entrainer, (*n*-butanol, b.p. 117 °C, forms azeotrope with water at 93 °C) is a highly efficient means for elimination of water without the need of rigorous operating conditions. In this study, nano-sized Al_2O_3–$2SiO_2$ powder was prepared by a sol–gel method, followed by azeotropic distillation for removal of water.

2. Experimental

Starting materials for the sol–gel syntheses are tetraethylorthosilicate (TEOS) and aluminium nitrate (ANN). Solvents

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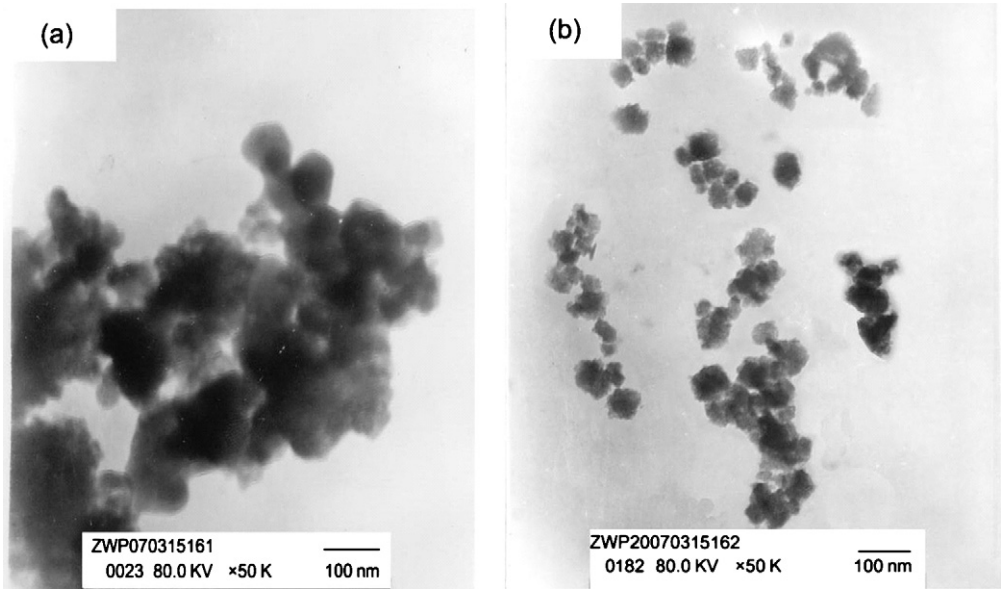

Fig. 1. TEM micrographs of the powder (a) by direct oven drying and (b) via azeotropic distillation.

for the syntheses are anhydrous ethanol and distilled water. Starting materials and solvents were mixed in the following ratios: 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 was maintained at 70 °C until a gel was formed. The gel was first dewatered at 93 °C (azeotropic point of water and *n*-butanol) for 2 h by azeotropic distillation with *n*-butanol, and then the temperature was increased to 117 °C to hold time for 0.5 h. The gel was dried in a microwave oven and crushed with a mortar and pestle. And the dry powder was calcined in air at 800 °C for 2 h.

A solution of sodium silicate (modulus, 2.8) and solid sodium hydroxide were mixed under stirring to make an activator solution (modulus, 1.2). The obtained activator solution was reacted with the prepared powder and distilled water by stirring, at molar ratios of $Al_2O_3/Na_2O = 1.0$, $H_2O/Na_2O = 10$ and $SiO_2/Al_2O_3 = 3.2$. The resulting resin was cast into unsealed 2.0 cm × 2.0 cm × 2.0 cm cubic moulds and cured at room temperature (about 28 °C) for 72 h. The cubes were then removed from the mould and tested for compressive strengths using a universal tester.

Infrared spectra of the powder 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 80° (2θ). An acceleration voltage of 40 kV and current of 10 mA were used. TEM examination was carried out with a TEM-1200EX/S transmission electron microscope at an accelerating voltage of 10 kV. The size distribution of the particles was measured by DTS (Zetasizer Nano-90). The specific surface area of the samples was examined with a Build SSA-3600 porosimetry analyzer. Simultaneously recorded TG/DTA studies of the powder were carried out using a STA-409PC thermal analyzer.

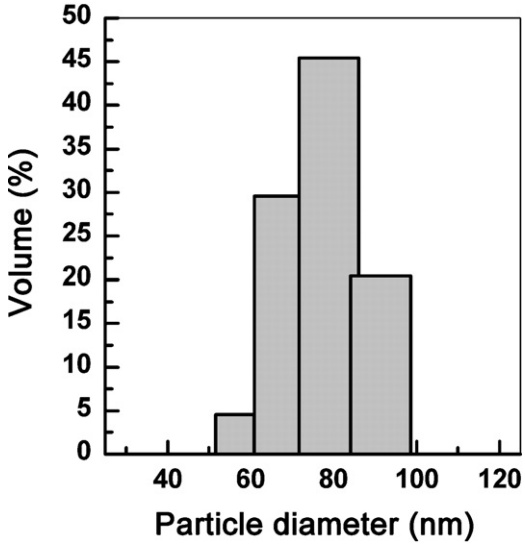

Fig. 2. Particle size distribution of the powder via azeotropic distillation.

3. Results and discussion

3.1. Particle size distribution and morphologies of the powder

The morphology of the powder and their particle size distribution are shown in Figs. 1 and 2. The samples via azeotropic distillation exhibit a sharp distribution of the particles (Figs. 1(b) and 2), with an average particle diameter of about 70 nm. The maximum specific surface area of the particles reaches 669 m^2/g (from BET analysis). However, the maximum specific surface area of the particles by direct oven drying is 208 m^2/g and their particle diameter is more than 100 nm (Fig. 1(a)).

Azeotropic distillation restrains the formation of hard agglomerates during the upcoming process of drying (Qiu, Gao, Feng, Guo, & Yan, 1994), because it can remove the free water in the wet colloid via the azeotrope. Therefore nanoparticles in this study were prepared via the azeotropic distillation process.

In oven drying, the free water molecules in the wet colloid interact with the free hydroxyls on the surface of the colloid particles through hydrogen bonds. Therefore, the free water molecules tend to draw neighboring particles if the particles get close enough. When the gel begins to dry these water molecules could be