



Alkali-activation reactivity of chemosynthetic Al_2O_3 – 2SiO_2 powders and their ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance spectra



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ABSTRACT

Pure Al_2O_3 – 2SiO_2 powders were prepared by sol–gel and coprecipitation methods, and their alkali-activation reactivities were compared. The alkali-activation reactivity of the powder prepared by the sol–gel method was higher than that of the powder prepared by the coprecipitation method. The powders were investigated by ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) to understand the relationship between their structure and alkali-activation reactivity. The ^{27}Al MAS NMR data showed that the five-coordinate Al content of the powder prepared by the sol–gel method was higher than that of the powder prepared by coprecipitation. The higher content of five-coordinate Al corresponded to higher alkali-activation reactivity. The ^{29}Si MAS NMR data showed that for the powder prepared by the sol–gel method, silicon was replaced by aluminum at secondary coordination sites of the central Si atoms during calcination. However, for the powder prepared by single-batch coprecipitation, the main change was from a low degree of polycondensation to a high degree of polycondensation.

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Introduction

Inorganic polymers have attracted considerable attention as novel materials. In this class of compounds, geopolymers are three-dimensional aluminosilicate mineral polymers that contain a variety of amorphous to semicrystalline phases. Geopolymers were first described by Davidovits (1988a). They exhibit excellent physical and chemical properties, such as high compressive strength, low shrinkage, and fast or slow setting times. These properties make them useful in a diverse range of potential applications, including immobilization of toxic, hazardous, and radioactive wastes, and use in advanced structural tooling and refractory ceramics (Davidovits, 1988a, 1988b, 1991; Van Jaarsveld et al., 1997).

Raw materials for producing geopolymers can be industrial wastes, such as fly ash and blast furnace slag, or natural minerals, such as kaolin (or metakaolin) and albite. Usually, natural metakaolin is fabricated from kaolin by a calcination process at

600–900 °C (Fletcher, MacKenzie, Nicholson, & Shimada, 2005; Palomo et al., 1999; Rahier, Simons, Van Mele, & Biesemans, 1997). Metakaolin is a good raw material for making high-strength geopolymers, which are often used in bioactive materials and fire-resistant materials. However, the chemical composition of natural kaolin is complex, and its Si/Al molar ratio is not fixed because of differences in the age of formation and the location of the kaolin mines. This affects the composition of metakaolin formed from kaolin.

The sol–gel approach is a cheap and low-temperature technique that allows for fine control of the product's chemical composition. It can be used in the manufacturing of many materials, such as nanomaterials, glass, ceramics, and very thin metal oxide films (Halbedel & Kontogeorgakos, 2007; Ma et al., 2014; Mackenzie, 1982; Whitesides, Mathias, & Seto, 1991). Oxides of Al–Si can also be prepared by the sol–gel method, but they are usually used to manufacture mullite (Bodart, Parmentier, Harris, & Thompson, 1999; Chen & Gu, 2008; Schmucker & Schneider, 1999). Considering the advantages and extensive applications of the method, pure Al_2O_3 – 2SiO_2 powders were prepared by the sol–gel method. The related geopolymers synthesized from them exhibited

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alkali-activation reactivity (Zheng, Cui, Zhang, & Tong, 2007; Zheng, Cui, Zhang, & Tong, 2009).

Alternatively, chemical coprecipitation is a common method of chemosynthesis. Because of its low cost and ease of operation, this method can be used for comparatively large-scale production. It is an economically efficient and easy process for the mass production of powders that possess alkali-activation reactivity. As a result, it may have practical significance as an industrial method for preparing starting materials for geopolymers.

Alkali-activation reactivity is one of the most important properties of the powders produced by these different methods. Therefore, in this study, the alkali-activation reactivities of pure Al_2O_3 - 2SiO_2 powders prepared by sol-gel and coprecipitation methods were compared. The structural features of the powders were studied by magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR).

Experimental

Preparation of Al_2O_3 - 2SiO_2 powders

The sol-gel method

Starting materials for the sol-gel syntheses were tetraethylorthosilicate (TEOS) (Xilong Chemical Co., Ltd, Guangdong, China) and aluminum nitrate nonahydrate (ANN) (Xilong Chemical Co., Ltd, Guangdong, China). Solvents for the synthesis were anhydrous ethanol (EtOH) (Xilong Chemical Co., Ltd, Guangdong, China) and distilled water. The molar ratio of Al_2O_3 to SiO_2 in the starting materials was determined in reference to the ideal chemical composition of metakaolinite. Considering that the relative amounts of starting materials with respect to solvents have been shown to have little effect on the alkali-activation reactivity of the powders (Zheng, 2011, chap. 3), the amounts of solvents used were not an important parameter for control. Thus, the minimal volume of each solvent was added to ensure sufficient EtOH was added to decrease the hydrolysis rate of TEOS and avoid precipitation, and sufficient water was added to favor dissolution of ANN. The 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 : H_2O :EtOH was 1:18:12. In a typical synthesis, two solutions were prepared with stirring: solution A, TEOS dissolved in EtOH; and solution B, ANN 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 for 12 h. After that, the dried product was calcined in air at 200, 300, 400, 500, 600, 700, or 800 °C for 2 h to yield the calcined powders. Finally, the dried product and calcined powders were milled and sieved through a 75- μm mesh sieve.

Coprecipitation method

To enable comparison of the products, the starting materials, solvents, and molar ratios for TEOS, ANN, EtOH, and water in the coprecipitation method were the same as those used in the sol-gel method. The dissolution and mixing steps were also the same. The resulting mixture was added to ammonium hydroxide (Xilong Chemical Co., Ltd, Guangdong, China) either by dropwise addition at a rate of 2 mL/min or in a single-batch addition (i.e. all at one time). The resulting precipitates were dried, calcined, milled, and sieved, as in the sol-gel method, to make the Al_2O_3 - 2SiO_2 powders.

Preparation of geopolymers

A solution of sodium silicate (modulus = 2.8, 'modulus' means its SiO_2 : Na_2O molar ratio) (Nanning Chunxu Chemical Co., Ltd, Guangxi, China) and solid sodium hydroxide (Xilong Chemical Co.,

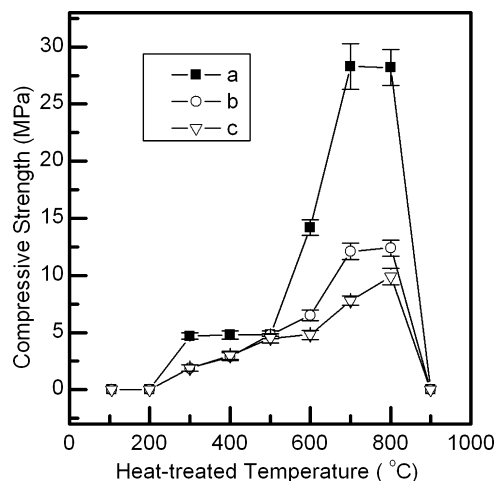


Fig. 1. Effect of the powder preparation method on the compressive strength: (a) sol-gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

Ltd, Guangdong, China) was mixed while stirring to make an activator solution (modulus = 1.2), which was reacted with the prepared powders and adequate distilled water while stirring. The molar ratios were 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 molds and cured at about 28 °C for 72 h. The cubes were then removed from the mold and tested for compressive strength using a universal tester (WDW-M50, Beijing Time High Technology Co., Ltd, Beijing, China). Three cubes were tested for each sample at a crosshead speed of 1 mm/min.

Characterization

^{29}Si and ^{27}Al NMR spectra were obtained on a Bruker AV300 NMR spectrometer (Germany) with a 4-mm probe 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, and referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. For ^{29}Si , the NMR conditions were 59.6 MHz resonance frequency, a 1.9- μs pulse width, a 15-s delay, and referenced to tetramethylsilane. The size distribution of the particles was measured by dynamic light scattering (DTS) (Zetasizer Nano-90, Malvern Instruments, UK).

Results and discussion

Effect of powder preparation method on alkali-activation reactivity

The compressive strengths of the cubes prepared with the powders fabricated by different methods reflect their alkali-activation reactivity. The effects of the different powder preparation methods on their alkali-activation reactivity are shown in Fig. 1.

These data show that the products calcined at temperatures ≤ 200 °C were not strong. Small strength increases were observed for the three materials calcined at temperatures between 300 and 500 °C. At temperatures between 600 and 800 °C the strength increased greatly, especially for the material produced by the sol-gel method. The alkali-activation reactivity results for powders prepared by the sol-gel method were much higher than those for powders prepared by the coprecipitation method. For the coprecipitation method, the alkali-activation reactivity results of powders prepared by dropwise addition were slightly higher than those

for powders prepared by the single batch addition. At 900 °C, the strength was lost for all materials.

In the proposed sol–gel reaction, a hydrolysis reaction of TEOS with water occurs first (Assink & Kay, 1988; Ro & Chung, 1989):

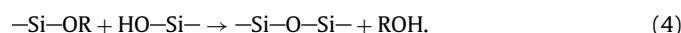
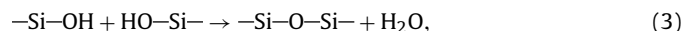


where $n = 1, 2, 3$, or 4 , and $\text{R} = \text{C}_2\text{H}_5$. This hydrolysis may proceed to completion with all of the OR groups replaced by OH groups, as follows:

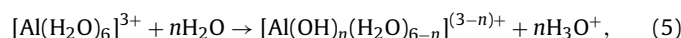


while any intermediate species $[(\text{OR})_2\text{Si}(\text{OH})_2]$ or $[(\text{OR})_3\text{Si}(\text{OH})]$ are the result of partial hydrolysis.

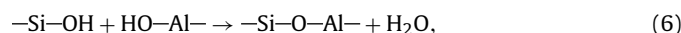
Then two hydrolyzed molecules or TEOS and a hydrolyzed molecule can link together via condensation reaction to form a $[\text{Si}-\text{O}-\text{Si}]$ bond, liberating water or ethanol:



When the soluble salt aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) is dissolved in water, the resulting aluminum ion is hydrated with water molecules to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ units. These release the hydronium ion to maintain the coordination number as follows:



where $n = 1, 2$, or 3 . These aluminum compounds can react with the silicon compounds produced in Eq. (1), resulting in the liberation of water:



producing a gel containing $[-\text{Si}-\text{O}-\text{Al}-]$ segments (Jones, Pritchard, & Lander, 1995). Therefore, both $[-\text{Si}-\text{O}-\text{Al}-]$ and $[-\text{Si}-\text{O}-\text{Si}-]$ segments are present in the gel prepared by the sol–gel method.

In the coprecipitation process, the reaction system becomes alkaline after the addition of ammonium hydroxide. Under alkaline conditions TEOS rapidly forms SiO_2 and $\text{Al}(\text{NO}_3)_3$ forms $\text{Al}(\text{OH})_3$, which means the products generated by coprecipitation are mainly SiO_2 and $\text{Al}(\text{OH})_3$ precipitates. As a result, $[-\text{Si}-\text{O}-\text{Al}-]$ segments are formed more easily and in greater numbers by the sol–gel method than by the coprecipitation method. Actually, the $[-\text{Si}-\text{O}-\text{Al}-]$ segments are closer to geopolymers in structure, therefore, the $[-\text{Si}-\text{O}-\text{Al}-]$ segments in the powders may favor the formation of geopolymers when the powders are alkali-activated. Therefore, the alkali-activation reactivity of powder prepared by the sol–gel method is obviously higher than those of powders prepared by the coprecipitation method.

The differences in the alkali-activation reactivity results for the powders prepared by the two methods of coprecipitation – dropwise and single-batch addition – can be understood by similar reasoning. In dropwise addition, ammonium hydroxide may have time to disperse into the solution, and TEOS and aluminum nitrate can produce $[-\text{Si}-\text{O}-\text{Al}-]$ segments. By contrast, in a single-batch addition, large quantities of SiO_2 and $\text{Al}(\text{OH})_3$ precipitates are generated, resulting in fewer $[-\text{Si}-\text{O}-\text{Al}-]$ segments in the powders prepared. As a result, the alkali-activation reactivity of the powder prepared by dropwise addition is higher than that for powder prepared by single-batch addition.

NMR spectra

The ^{27}Al MAS NMR spectra of the powders prepared by different methods and dried at 105 °C are shown in Fig. 2. Each spectrum showed two signals centered at about 1 and 55 ppm, which

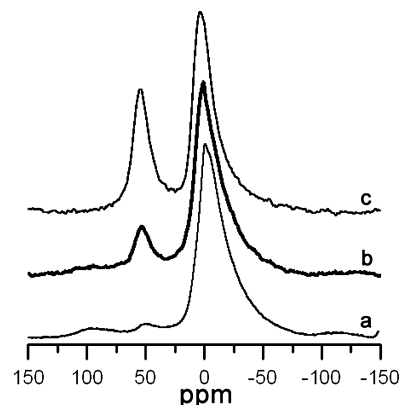


Fig. 2. ^{27}Al MAS NMR spectra of the powders prepared by different methods after drying at 105 °C: (a) sol–gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

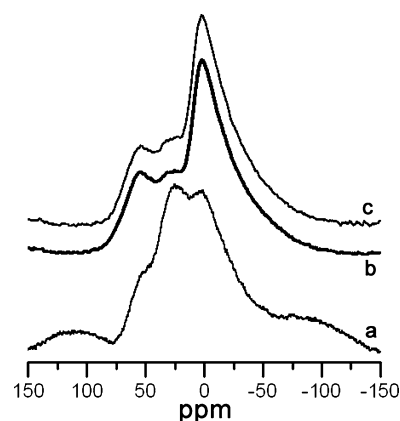


Fig. 3. ^{27}Al MAS NMR spectra of the unactivated powders prepared by different methods and calcined at 800 °C: (a) sol–gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

Table 1

Percentages of Al(IV), Al(V), and Al(VI) in the different powders obtained by integration as the proportion of the area under the curve in the spectra in Fig. 3.

Method	Percentage of integrated area		
	Al(IV)	Al(V)	Al(VI)
Sol–gel	6.1	49.6	44.4
Dropwise addition coprecipitation	18.3	14.1	67.6
Single-batch addition coprecipitation	15.9	14.2	69.9

were assigned to six-coordinate Al [Al(VI)] and four-coordinate Al [Al(IV)], respectively. The content of six-coordinate Al was obviously greater than that of four-coordinate Al in each spectrum. The content of four-coordinate Al in the powders prepared by single-batch coprecipitation was higher than that in the powders prepared by dropwise coprecipitation and by the sol–gel method.

The ^{27}Al MAS NMR spectra of the powders prepared by different methods and calcined at 800 °C are shown in Fig. 3. Each spectrum showed three signals centered at about 1, 25, and 55 ppm, which were assigned to six-coordinate Al, five-coordinate Al [Al(V)], and four-coordinate Al, respectively. Using Origin software, through Gaussian fitting, the areas under the curves for the peaks in the spectra of the samples calcined at 800 °C were obtained by integration, and used to calculate the percentages of different coordinate Al peaks (Table 1). The content of Al(V) in the powder prepared by the sol–gel method was much greater than those in the powders prepared by coprecipitation (single-batch and dropwise). As

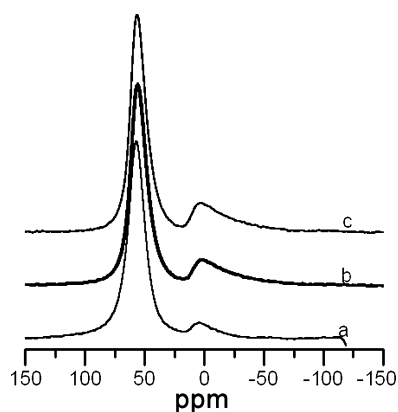


Fig. 4. ^{27}Al MAS NMR spectra of the alkali-activated powders prepared by different methods and calcined at 800°C : (a) sol-gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

shown in Table 1, the Al(V) contents of the peak prepared by dropwise and single-batch coprecipitation were similar. Therefore, the Al(V) contents of the powders after calcination may be related to the contents of the $[-\text{Si}-\text{O}-\text{Al}-]$ segments in the powders before calcination. In addition, the Al(V) contents of the powders prepared by these different methods are in agreement with their alkali-activation reactivities, as reflected in the compressive strengths of the cubes prepared with the different powders (Fig. 1). Rocha and Klinowski (1990) believed that Al(V) was the principal indicator of the reactivity of a material and that it characterized a transitional state. The peak strengths attributed to Al(V) were consistent with this suggestion.

The formation of Al(V) in the calcined samples arises from the dehydroxylation of Al(VI) in the dried powders (Mackenzie, Brown, Meinhold, & Bowden 1985; Taylor & Holland, 1993). As mentioned in Section ‘Effect of powder preparation method on alkali-activation reactivity’, in addition to oxygen atoms, aluminum atoms are coordinated to hydroxyl groups in the sol-gel process. Thus, Al(V) in the calcined samples is formed by thermal decomposition through the elimination of water from neighboring hydroxyl groups.

The reactivity of a powder usually increases as its particle size decreases. However, it was unclear how much this influenced the powders prepared in this study. Therefore, the particle sizes of powders prepared by different methods and calcined at 800°C were determined by DTS. The D_{50} of the powders prepared by sol-gel, dropwise addition coprecipitation, and single-batch addition coprecipitation were about 220, 310, and 190 nm, respectively. The alkali-activation reactivity results for the powders prepared by the different methods were not consistent with their particle sizes according to these data and the data from Fig. 1. This shows that the particle size of the powder has less influence on the reactivity than the five-coordinate Al content.

The ^{27}Al MAS NMR spectra of the alkali-activated samples of the powders prepared by different methods and calcined at 800°C are shown in Fig. 4. Each spectrum showed two signal peaks, with one centered at about 1 ppm for Al(VI) and the other centered at about 55 ppm for Al(IV). After the alkali-activation reaction, Al(V) and Al(VI) were converted to Al(IV) and the broad spectral peaks sharpened into well-defined peaks, which is characteristic of geopolymers (Duxson et al., 2007; Singh, Bastow, & Trigg, 2005).

The areas under the curves for the peaks in the spectra of the samples calcined at 800°C were determined, and the percentages of different coordinate Al peaks were calculated (Table 2). The Al(VI) content in the powder prepared by the sol-gel method was less than those in the powders prepared by coprecipitation. The data in

Table 2

Percentages of Al(IV) and Al(VI) in the different powders obtained by integration as the proportion of the area under the curve in the spectra in Fig. 4.

Method	Percentage of integral area	
	Al(IV)	Al(VI)
Sol-gel	91.2	8.8
Dropwise addition coprecipitation	77.5	22.5
Single-batch addition coprecipitation	78.1	21.9

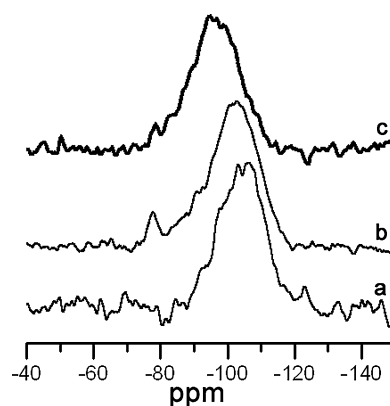


Fig. 5. ^{29}Si MAS NMR spectra of the powders prepared by different methods and dried at 105°C : (a) sol-gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

Table 2 also show that the Al(VI) content of the powder prepared by dropwise coprecipitation was similar to that in the powder prepared by single-batch coprecipitation. These data show that more Al conversion took place in the powder prepared by the sol-gel method than in the powders prepared by coprecipitation. In addition, the alkali-activation reactivity of the powder prepared by the sol-gel method was higher than those of the powders prepared by coprecipitation.

Silicate structures may be regarded as being built up of tetrahedral units with varying degrees of polymerization. These can be described in terms of a ‘Q’ notation, where Q denotes a silicon atom bonded to four oxygen atoms. The number of other units attached to the unit in question is indicated by the superscript n ($n=0$ to 4). Thus, Q^0 denotes a silicon bonded through oxygen to no other network-forming elements, Q^1 denotes a silicon bonded through oxygen to one other silicon, Q^2 denotes a silicon bonded through oxygen to two other silicon atoms, and so on. The silicon of the Q unit in question is called the central silicon atom. For aluminosilicate structures, the notation $Q^n(m\text{Al})$ ($0 \leq n \leq 4$) is used, where n is the number of T (Si or Al) atoms bonded through oxygen to the central Si atom and m is the number of Al atoms bonded through oxygen to the central Si atom. This notation is used to describe the connectivity of a silicon tetrahedron bridged through oxygen to aluminum and to other silicon centers. For example, $Q^4(1\text{Al})$ denotes a silicon bonded through oxygen to a Al atom and to three other Si atoms (Duxson, 2006, chap. 2; MacKenzie & Smith, 2002).

The ^{29}Si MAS NMR spectra of the powders prepared by different methods and dried at 105°C are shown in Fig. 5. The peak center of the spectrum of powder prepared by the sol-gel method was at about -104.5 ppm. According to our previous research (Zheng et al., 2009), the spectrum may be assigned to a mixture of $Q^4(m\text{Al})$ and $Q^3(m\text{Al})$ structures. The center values of the spectra of powders prepared by coprecipitation were at about -102 ppm for the dropwise coprecipitation (spectrum b), and about -96 ppm for the single-batch coprecipitation (spectrum c). MacKenzie and Smith (2002)

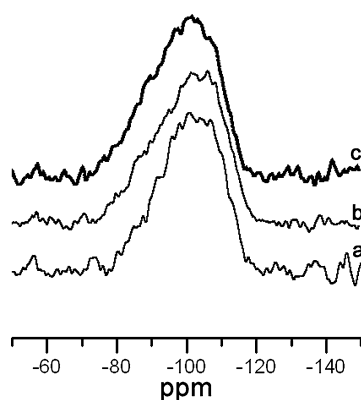


Fig. 6. ^{29}Si MAS NMR spectra of the unactivated powders prepared by different methods and calcined at 800°C : (a) sol-gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

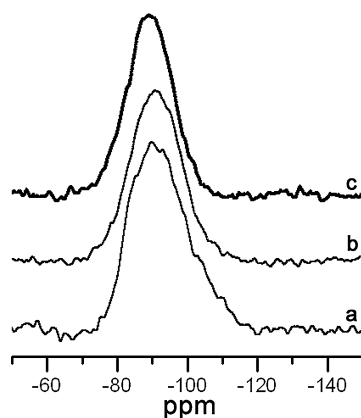


Fig. 7. ^{29}Si MAS NMR spectra of the alkali-activated powders prepared by different methods and calcined at 800°C : (a) sol-gel method, (b) dropwise addition coprecipitation, and (c) single-batch addition coprecipitation.

presented the chemical shifts for ^{29}Si NMR of silicates and aluminosilicates. Referring to their research, the spectrum centered at about -102 ppm for the dropwise coprecipitation can be assigned to $\text{Q}^3(\text{mAl})$ and $\text{Q}^4(\text{mAl})$. Similarly, the one at about -96 ppm for the single-batch coprecipitation can be assigned to $\text{Q}^2(\text{mAl})$, $\text{Q}^3(\text{mAl})$, and a small quantity of $\text{Q}^4(\text{mAl})$.

The ^{29}Si MAS NMR spectra of the powders prepared by different methods and calcined at 800°C are shown in Fig. 6. The spectra showed a resonance center at about -101 ppm for the sol-gel and dropwise coprecipitation powders, and at about -99 ppm for the single-batch coprecipitation powder. Based on our previous research (Zheng et al., 2009), each peak may be assigned to a mixture of $\text{Q}^4(\text{mAl})$ and $\text{Q}^3(\text{mAl})$ structures.

The ^{29}Si MAS NMR spectra of alkali-activated powders prepared by different methods and calcined at 800°C are shown in Fig. 7. The spectra showed a peak center at about -91 ppm for the sol-gel and dropwise coprecipitation powders, and at about -89 ppm for the single-batch coprecipitation powder. It has been observed that ^{29}Si MAS NMR spectroscopy of fully cured geopolymers show a broad signal band in the region from -85 to -95 ppm (Duxson, Provis, Lukey, Separovic, & Van Deventer, 2005; Singh et al., 2005). Therefore, these spectra (Figs. 6 and 7) indicate that geopolymerization has occurred.

Gaussian fitting of the spectra in Figs. 5–7 using Origin software was applied to determine the centers of the signals (Table 3). The chemical shifts of Gaussian-fitted peaks from the ^{29}Si NMR spectra of powders before and after calcination and alkali-activated

Table 3

Chemical shift of Gaussian peak fitting for the spectra in Figs. 5–7.

Method	Chemical shift of Gaussian fitting peak (ppm)		
	Powders dried at 105°C	Powders calcined at 800°C	Alkali-activated powders
Sol-gel	-104.4	-101.5	-91.6
Dropwise addition coprecipitation	-102.1	-101.1	-91.1
Single-batch addition coprecipitation	-96.2	-99.4	-89.3

products reflected changes in the molecular structures of the samples. Dehydration of powders, that is, the dehydroxylation of powders (calcination process), will result in central Si atoms with more T (Si or Al) atoms around them at secondary coordination sites, which means there will be changes from Q^0 to Q^1 , Q^1 to Q^2 , Q^2 to Q^3 , or Q^3 to Q^4 . This would lead to an upfield shift. For example, when kaolin changes to metakaolin during calcination, an upfield shift from -91 to -103 ppm occurs (Singh, Bastow, & Trigg, 2005). The chemical shift for powders from single-batch coprecipitation (from -96.2 to -99.4 ppm, as shown in Table 3) was consistent with that of kaolin-to-metakaolin during calcination. However, the chemical shifts for both the sol-gel and dropwise coprecipitation samples were not consistent with that of kaolin-to-metakaolin during calcination. A downfield shift from -104.4 to -101.5 ppm was observed for the sol-gel product, and from -102.1 to -101.1 ppm for the dropwise coprecipitation product (see Table 3). According to MacKenzie and Smith (2002), the replacement of one silicon with one aluminum at a given site causes a downfield shift of about 5 ppm. Therefore, there must be some replacement of silicon with aluminum for the powders produced by the sol-gel and dropwise coprecipitation methods during calcination. As the aluminosilicate structures in the powders from the sol-gel method are mainly Q^3 and Q^4 , the effects of replacing silicon with aluminum on the chemical shift will be greater than those for changes from Q^1 to Q^2 , Q^2 to Q^3 , or Q^3 to Q^4 . Then, the chemical shift is from -104.4 to -101.5 ppm, that is, a downfield shift. For dropwise coprecipitation, the powders mainly contain Q^3 and Q^4 aluminosilicate structures, but the quantities of Q^3 and Q^4 are less than those in the sol-gel powders. Correspondingly, the effect of replacing silicon with aluminum on the chemical shift for dropwise coprecipitation is less than that observed for the sol-gel method. Therefore, a small downfield shift was observed for the chemical shift for dropwise coprecipitation from -102.1 to -101.1 ppm. In the case of single-batch coprecipitation, the powder mainly contains Q^2 and Q^3 aluminosilicate structures, with a small quantity of Q^4 . Therefore, the effect of replacing silicon with aluminum on the chemical shift will be less than that for the change from Q^1 to Q^2 , Q^2 to Q^3 , or Q^3 to Q^4 . An upfield chemical shift was observed from -96.2 to -99.4 ppm. As a result, for the powders prepared by the sol-gel method, there is an obvious replacement of silicon with aluminum at secondary coordination sites of the central Si atoms during calcination of the powders. However, the main change for the single-batch coprecipitation method is from Q^1 to Q^2 , Q^2 to Q^3 , or Q^3 to Q^4 .

Conclusions

Pure $\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$ powders for geopolymer formation were prepared by sol-gel and coprecipitation methods. The alkali-activation reactivity results of the powders prepared by the sol-gel method were higher than those for the powders prepared by the coprecipitation method. For the coprecipitation method, the

alkali-activation reactivity results of the powders prepared by dropwise addition were slightly higher than those for powders prepared by single-batch coprecipitation. Although the alkali-activation reactivity results of the powders prepared by the coprecipitation method were low in comparison to the sol–gel method powders, the coprecipitation powders may be favored for situations where high strength is not required because of the low cost and high economic efficiency associated with this method.

By ^{27}Al MAS NMR analysis, the contents of five-coordinate aluminum in the powders prepared by the sol–gel method were higher than those prepared by the coprecipitation method, and this is in agreement with their alkali-activation reactivity. This is further verification that five-coordinate aluminum is a principal indicator of the alkali-activation reactivity.

For the powders prepared by the sol–gel method, ^{29}Si MAS NMR analysis revealed that silicon was replaced by aluminum at secondary coordination sites of the central Si atoms during calcination of the powders. By contrast, the main change for the single-batch addition coprecipitation sample was from Q^1 to Q^2 , Q^2 to Q^3 , or Q^3 to Q^4 .

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