

^{27}Al and ^{29}Si MAS–NMR studies of structural changes in hybrid aluminosilicate gels

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Abstract

Aluminosilicate gels with stoichiometric and nonstoichiometric compositions were synthesized by means of colloidal sol-gel method and their mullitization behavior was studied by X-ray diffraction (XRD), ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS–NMR) experiments. Particular attention was given to the structural changes of matrix accompanying the formation of mullite. The various coordinated Al occupancies were clarified by simulating the ^{27}Al MAS–NMR spectra with Gaussian lines. The results demonstrate that the so-synthesized aluminosilicate gel is a hybrid gel containing a mixture of a single-phase gel and a diphasic gel. The mullitization of so-formed hybrid gel exhibits a consecutive one-step conversion process, but not a two-step process, much similar to that of a true diphasic mullite gel. The mullite formation from hybrid aluminosilicate gel mainly depends on the nature of dominant matrix part, but not on the nature of minor matrix part in gel. During the formation process of mullite, amorphous Si-rich phase appears as a transitional phase. The effects of gel composition and heating rate on the phase transformation behavior of hybrid aluminosilicate gel were also discussed here. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Due to its high purity, good homogeneity and high reactivity, chemically derived mullite has received much attention during the last 20 years. The mechanism and behavior of mullite crystallization from single-phase and diphasic aluminosilicate gels have been thereby studied by numerous investigators. Al-Jarsha et al.¹ prepared a dozen gels from ethyl silicate and aluminum chloride to determine the effects of organic and inorganic additives in the gels on the mullite conversion. By ^{27}Al magic angle spinning nuclear magnetic resonance (MAS–NMR), Sanz et al.² studied the structural changes of diphasic gel on heat-treatment and demonstrated that the segregation of Al_2O_3 and SiO_2 also took place in polymeric gels prior to the formation of mullite. The study by Li and Thomson³ showed that the dissolution and exsolution of alumina into or from mullite solid solution occurred on heating temperature in diphasic mullite gel with Al/Si atomic ratio of 6/1. Yoldas and Partlow⁴ examined the effects of precursors and preparation conditions on the structure of monophasic aluminosilicate gels. In studying

the effect of hydrolysis on the transformation kinetics of aluminosilicate gels, Li and Thomson⁵ found that the apparent single-phase aluminosilicate gel they prepared was in fact a composite of a single-phase gel and a diphasic gel, and the mullite formation from these composite gels was a two-stage conversion process.

Although many of those earlier works, there have been a limited number of reports concerning the detailed changes of local structure in hybrid aluminosilicate gel before and following the crystallization of mullite. The objective of this work is to investigate the mullitization behavior of hybrid aluminosilicate gels derived via colloidal sol-gel method by X-ray diffraction (XRD), ^{27}Al and ^{29}Si MAS–NMR techniques. The simulation and deconvolution of ^{27}Al MAS–NMR spectra have allowed the determination of structural changes accompanying the formation of mullite. Some attention was also paid to the effects of gel composition and heating rate of thermal treatment on the formation behavior of mullite.

2. Experimental procedure

Diphasic aluminosilicate gels with Al_2O_3 molar percents of 50, 60 and 70 were prepared by sol-gel method,

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labeled henceforth as M50, M60 and M70, respectively. Silica sol and alumina sol (all from Nissan Chemical Industries Ltd) were used as starting materials. A suitable amount of silica sol was gradually added to a measured quantity of alumina sol under vigorous stirring. The mixed solutions were aged at room temperature in air for 2–3 days and then slowly dried at 60 °C in a drier. During drying, the solution became concentrated and gradually turned into a glassy gel. The so-formed gels were calcined in air under two different thermal schedules: one is a rapid heating schedule (RH): heated at the rate of 7 °C/min up to the designed temperature directly and then kept at the temperature for 3 h; the other is a slow heating schedule (SH): heated at the rate of 2 °C/min to 500 °C and held at 500 °C for 2 h, then further heated at the rate of 5 °C/min up to the designed temperature and held at that temperature for 3 h.

XRD examination was carried out using a MXP 3VA X-ray diffractometer with Ni-filtered CuK_α radiation. The diffraction data were analyzed using XPRESS software developed by MAS science Co., Ltd and at the University of Oxford, and the standard diffraction data provided by the Joint Committee on Powder Diffraction Standards (JCPDS).

High-resolution solid-state MAS–NMR experiments were performed on a Varian UNITYINOVA 300 FT–NMR spectrometer, equipped with a CP/MAS probe. ^{29}Si MAS–NMR spectra were recorded at 7.05 T (tesla). The samples were placed in a zirconia sample tube 7 mm in diameter. The sample spinning speed at the magic angle to the external field was 5 kHz. ^{29}Si MAS–NMR spectra were taken at 59.6 MHz with 3.0- μs ($\text{pai}/2$) pulses, 120 s recycle delays where the signals from about 1000–3000 pulses were accumulated. The chemical shift is represented in CS (ppm) by convention. Polydimethylsilane (PDMS: –34.0 ppm against tetramethylsilane: 0 ppm) was used as the secondary external reference.

^{27}Al MAS–NMR spectra were also recorded at 7.05 T (tesla) on a Varian UNITYINOVA 300 FT–NMR spectrometer, equipped with a cp/MAS probe. The sample-spinning speed at the magic angle to the external field was 5 kHz. $[\text{Al}(\text{H}_2\text{O})]^{3+}$ (1 M $\text{Al}(\text{NO})_3$ solution) was used as the external reference (0 ppm).

3. Results and discussion

3.1. XRD results

The M60 sample with stoichiometric composition of 3:2 mullite was calcined under an SH condition at different temperatures ranging from 1000 to 1700 °C, then examined by powder XRD. Fig. 1 shows the results. Hereafter, unmarked peaks in XRD patterns represent the mullite phase.

Besides amorphous phase, only $\gamma\text{-Al}_2\text{O}_3$ and a small amount of $\theta\text{-Al}_2\text{O}_3$ can be detected in those samples calcined at 1000–1200 °C. The mullite crystalline commences to form at about 1300 °C, together with the presence of a relatively large amount of coexisting SiO_2 (cristobalite) and $\theta\text{-Al}_2\text{O}_3$ phases. The typical double peaks for orthorhombic mullite (120 and 210 at about 2θ) become obvious at 1400 °C. After being calcined at 1500 °C for 3 h, M60 sample shows a relatively remarkable double peaks with a considerably higher XRD intensity, while SiO_2 and Al_2O_3 phases ($\alpha\text{-Al}_2\text{O}_3$) still exist but just with relatively lower intensities. Mullitization can be achieved completely at 1600 °C, above which there is no impurity present.

In order to investigate the effect of heating rate on formation behavior of mullite, M60 sample was also subjected to an RH heat treatment at some selected temperatures. The powder XRD patterns are shown in Fig. 2. As can be seen, SiO_2 and Al_2O_3 phases are still detectable in samples even though the calcining temperature is up to as high as 1600 °C. The mullitization process can thoroughly take place only when the calcining temperature reaches or exceeds 1700 °C.

According to the above results, it is reasonable to state that the lower heating schedule is favorable for the extensive achievement of mullitization. Heating schedule plays an important role in the formation process of mullite, i.e. on which the formation temperature of mullite and its coexisting phases are strongly dependent.

Based on the XRD results of M60 gel, the experiments on M50 and M70 gels were only done under SH condition. The powder XRD patterns of M50 and M70 samples calcined at different temperatures are shown in Figs. 3 and 4, respectively. The typical double peaks for orthorhombic mullite are already distinguishable at 1300 °C in M50 sample when compared to M60 and M70 samples, with the simultaneous detection of $\theta\text{-Al}_2\text{O}_3$ and cristobalite phases. The peak intensities of Al_2O_3 and SiO_2 phases in M50 sample gradually decrease with increasing temperature and eventually disappear at 1600 °C, presumably due to the further combination of SiO_2 and Al_2O_3 components remained from gels to yield mullite crystalline. On the other hand, the formation of a Si-rich liquid phase above 1587 °C⁶ is considered to be another contribution to this phenomenon.

For M70 sample, mullite phase with indistinct double peaks appears at 1300 °C, accompanying a considerable amount of cristobalite, $\theta\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ phases, and a bit of amorphous phase. With the increase of temperature, $\theta\text{-Al}_2\text{O}_3$ gradually converts to $\alpha\text{-Al}_2\text{O}_3$ and then progressively reacts with SiO_2 component to form mullite lattice at higher temperature. The amorphous phase disappears at 1500 °C, but a large amount of cristobalite still coexists with mullite and $\alpha\text{-Al}_2\text{O}_3$ phases, although only mullite solid solution and $\alpha\text{-Al}_2\text{O}_3$ phases should be the equilibrium phases at that tem-

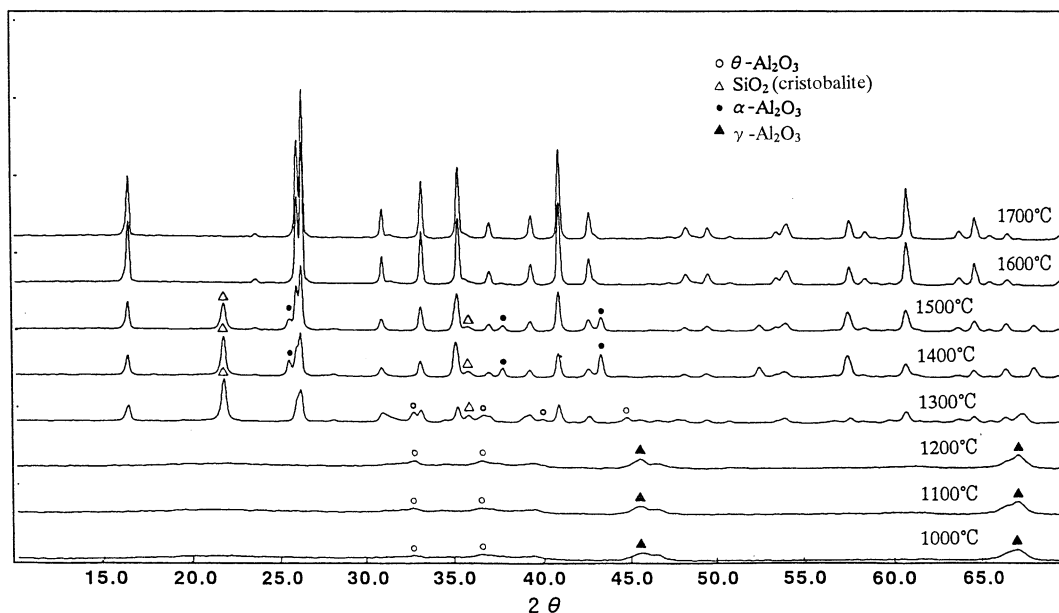


Fig. 1. XRD patterns of M60 sample calcined at different temperatures under an SH condition.

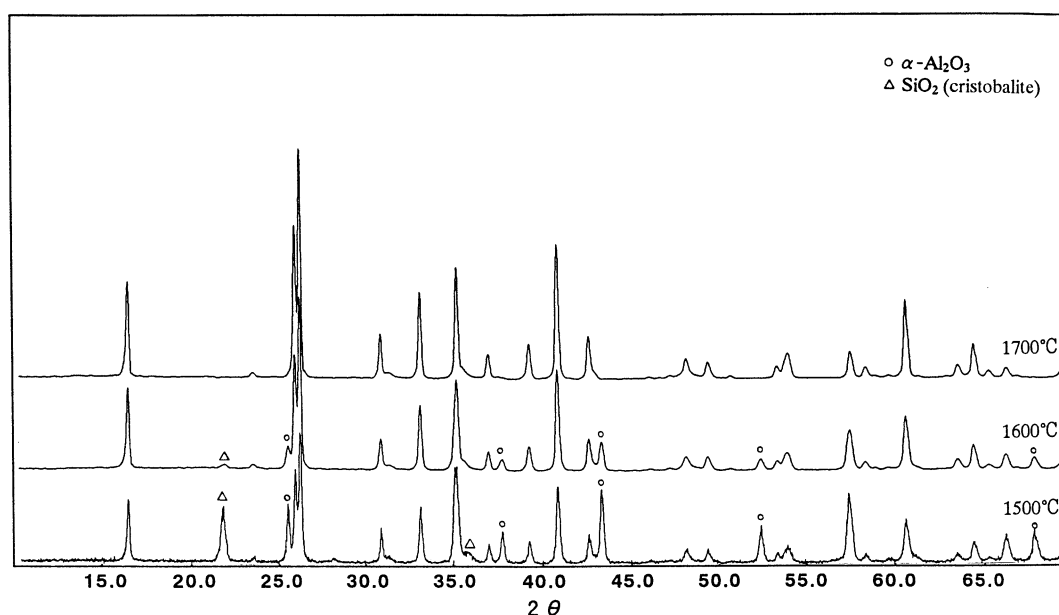


Fig. 2. XRD patterns of M60 sample calcined at different temperatures under an RH condition.

perature according to the phase diagram.⁶ This suggests that the mullitization from colloidal aluminosilicate gel is a slow process in kinetics. At 1700 °C, a certain amount of α - Al_2O_3 phase still remains in the sample because the Al_2O_3 content in M70 sample has exceeded the solid-solution limitation of Al_2O_3 in mullite lattice structure.

The above results indicate that the orthorhombic mullite directly crystallizes at ca. 1300 °C from colloidal aluminosilicate gels, quite different from that in polymeric aluminosilicate gels. The gel with excessive SiO_2 content compared with stoichiometric 3:2 mullite is relatively easier to form orthorhombic mullite than the

others. The reason remains unknown so far, thus more extensive study is surely needed.

3.2. ^{29}Si MAS-NMR

A fully condensed silicon atom connected via oxygen bridge to m Al atoms is labeled in here as $\text{Q}^4(m\text{Al})$, when m varies between 1 and 4, likewise a fully condensed silicon atom connected to four Si atom is denoted as $\text{Q}^4(0\text{Al})$.

The ^{29}Si MAS-NMR spectra of M50, M60 and M70 samples calcined at 700 °C are shown in Fig. 5. Almost

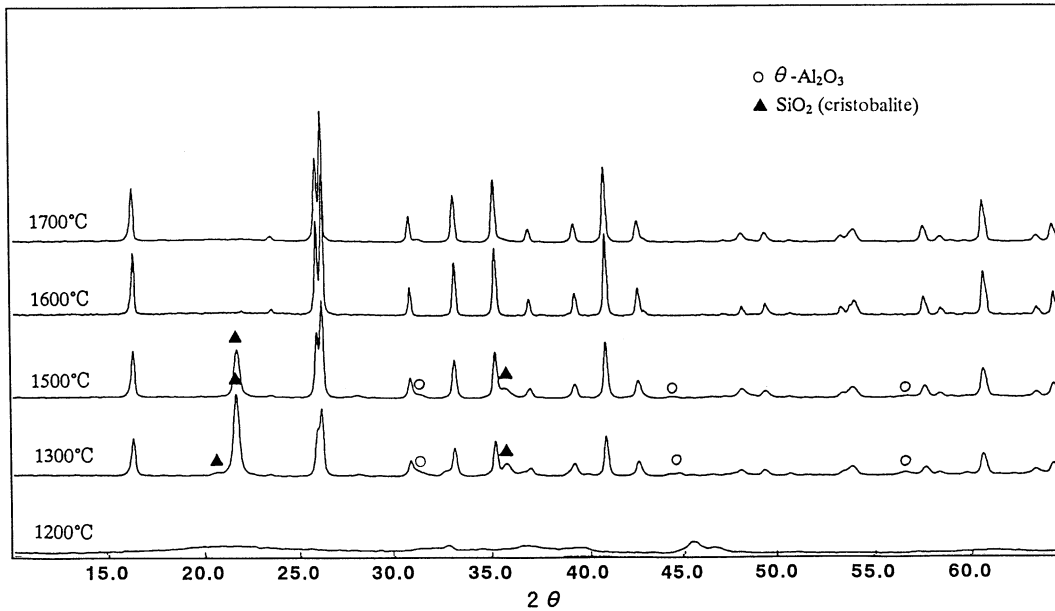


Fig. 3. XRD patterns of M50 sample heat-treated at different temperatures.

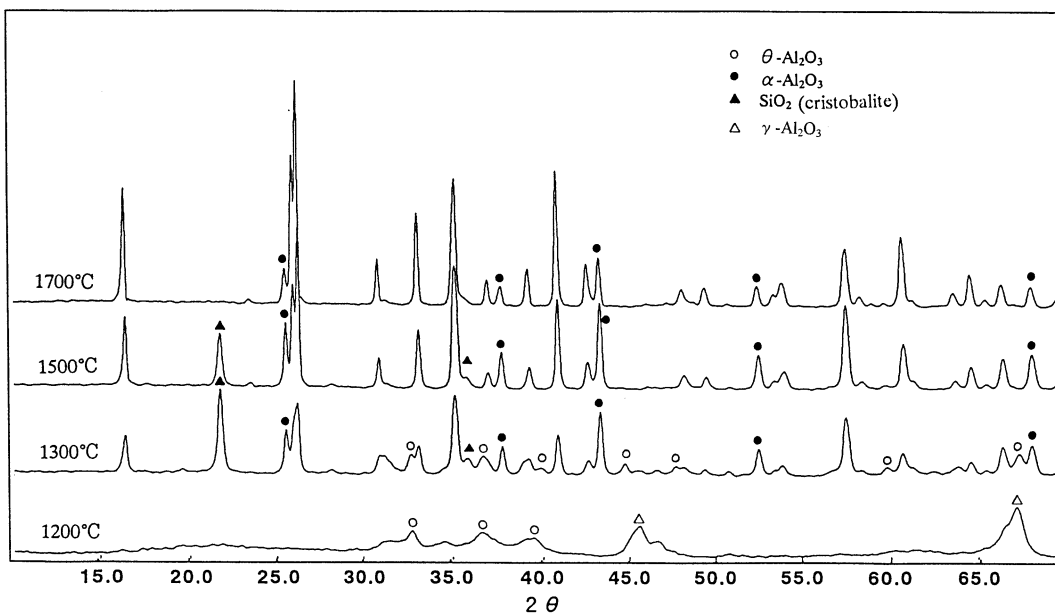


Fig. 4. XRD patterns of M70 sample heat-treated at different temperatures.

similar spectra have been obtained for these three samples. The free silica component is clearly identified by a characteristic resonance at ca. -110 ppm for all three samples, indicating the heterogeneity of matrix in silicon and aluminum distributions. Simultaneously, a broad and less intense resonance centered at ca. -82 ppm appears, attributable to the existence of Si in Al-rich $\text{Q}^4(4\text{Al})$ environment. This probably means that a small quantity of Si and Al atoms have already mixed homogeneously on an atomic level in the colloidal precursors, although the segregation of Al and Si atoms is important

in this case. The so-synthesized aluminosilicate gel is far more likely a hybrid gel composed of a single-phase gel and a diphasic gel.

Fig. 6 shows the ^{29}Si MAS-NMR spectra of M60 sample with stoichiometric ratio of 3:2 mullite calcined at different temperatures. The typical NMR peaks for mullite, centered at -86 , -90 and -94 ppm and with a shoulder at -80 ppm, are already quite clear at 1300°C and become much sharper at 1600°C , indicating the increasing degree of lattice order of mullite. The resonance centered at ca. -110 ppm tends to much sharper

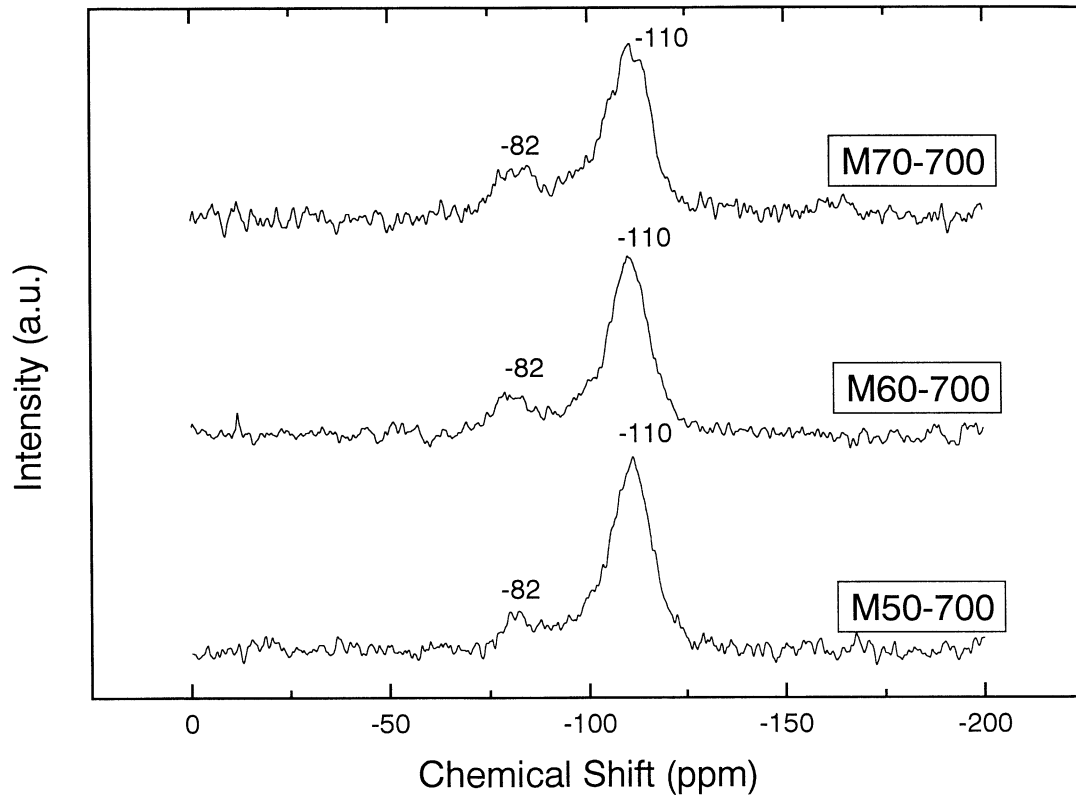


Fig. 5. ^{29}Si MAS-NMR spectra of the colloidal gels calcined at 700°C .

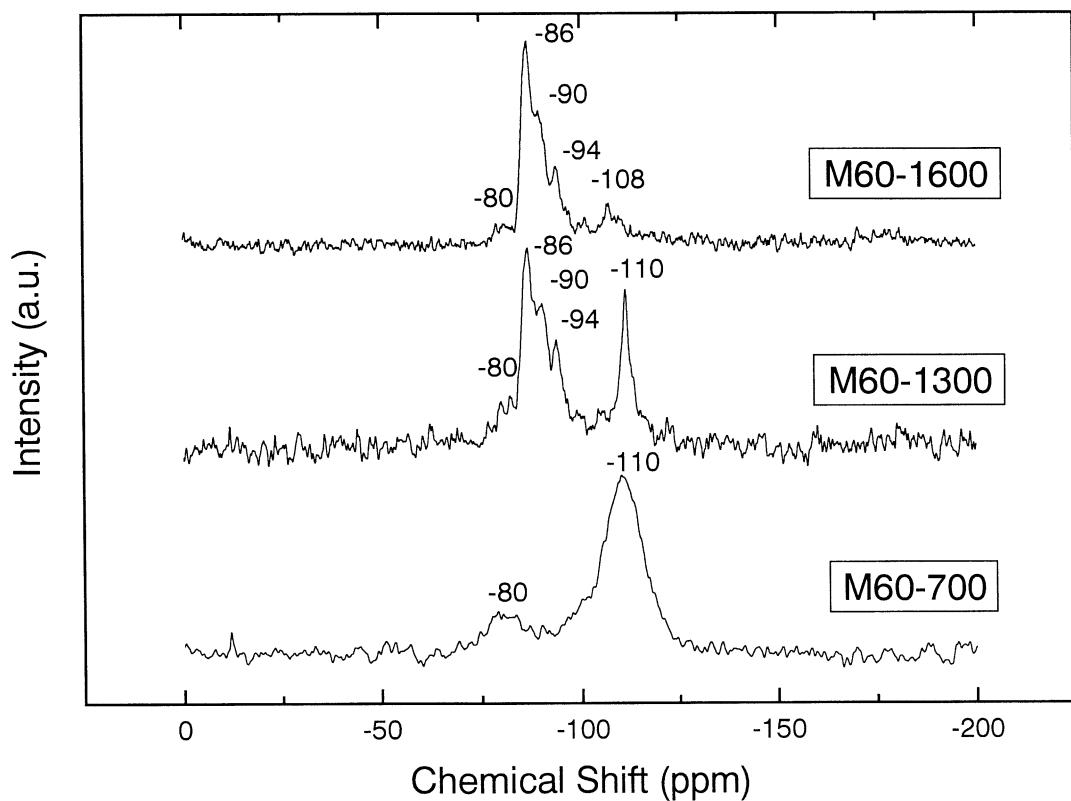


Fig. 6. ^{29}Si MAS-NMR spectra of M60 colloidal gel calcined at different temperatures.

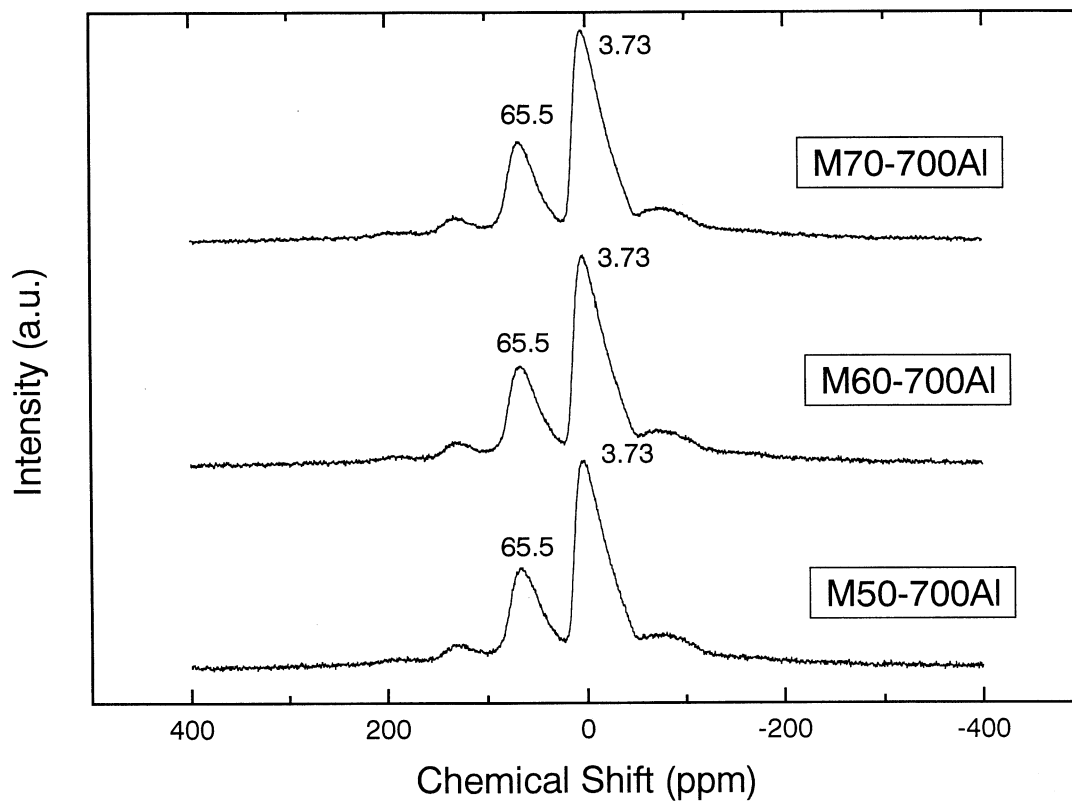


Fig. 7. ^{27}Al MAS-NMR spectra of colloidal aluminosilicate gel calcined at 700 °C.

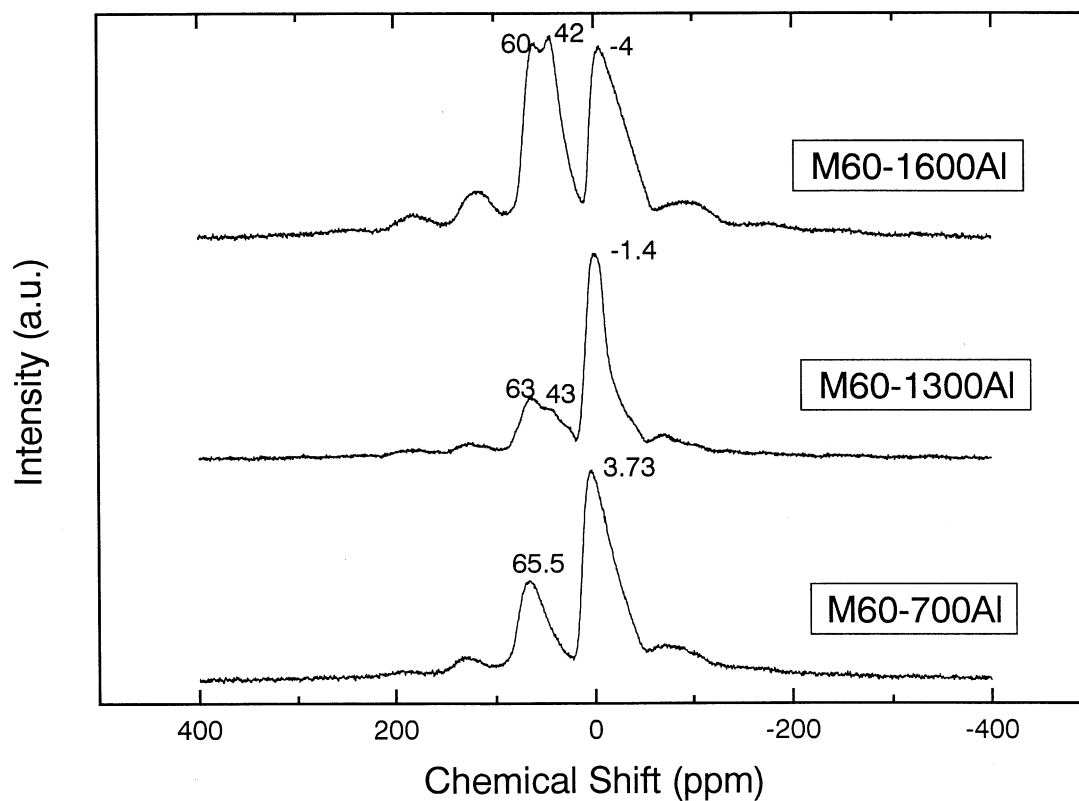


Fig. 8. ^{27}Al MAS-NMR spectra of M60 gel calcined at different temperatures.

at 1300 °C, but becomes weaker and shifts to –108 ppm at 1600 °C. This can be ascribed to the priority of crystallization of Al-rich mullite, some silicon atoms being always expelled during the process.⁷ The expelled silica component then progressively reincorporates into the mullite lattice in turn with increasing temperature, so resulting in the weakening of resonance at –110 ppm.

On the other hand, the sharpening of resonance at –110 ppm indicates the crystallization of SiO₂ component when compared with the broad one at 700 °C where the Si distribution is not so regular and some other kinds of coordinated state coexists with Q⁴(0Al) units in a relatively small quantity. The shift of resonance from –110 ppm to –108 ppm can be attributed to the formation of

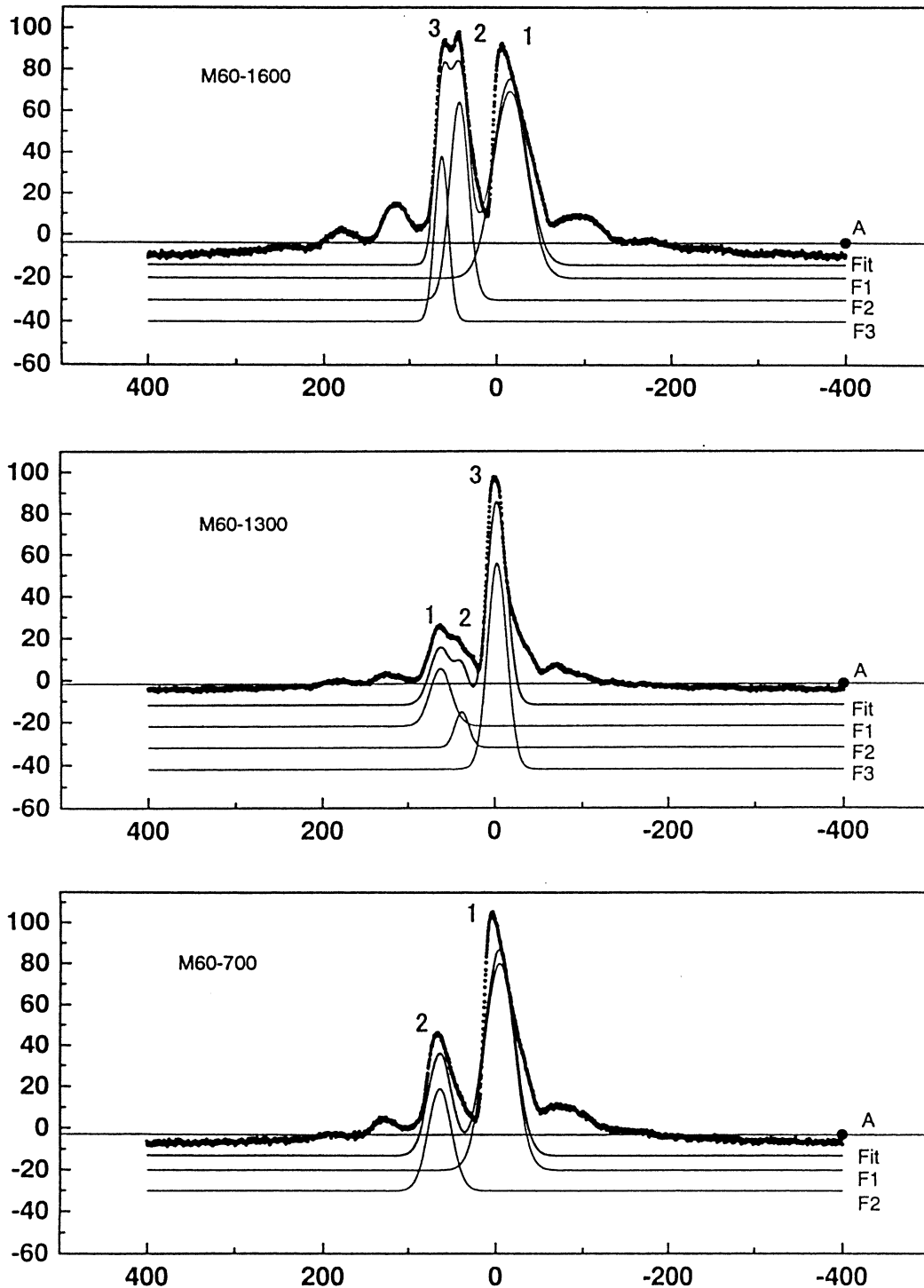


Fig. 9. Simulated ²⁷Al MAS-NMR spectra of M60 gel calcined at different temperatures.

$Q^4(1Al)$ pieces, which was considered to be a transitional phase during the dissolution process of SiO_2 crystalline into the initially formed mullite. This transitional phase should be an amorphous phase, as evidenced by the XRD analysis results, where SiO_2 phase can be detected at 1300–1500 °C but cannot at 1600 °C, as shown in Fig. 1.

3.3. ^{27}Al MAS–NMR

^{27}Al MAS–NMR measurement was also performed on M50, M60 and M70 samples calcined at different temperatures. Some ^{27}Al MAS–NMR spectra were fitted to a sum of Gaussian lines using a gradient minimization algorithm that optimizes position, width and amplitude of each line.

Fig. 7 shows the ^{27}Al MAS–NMR spectra for all investigated samples calcined at 700 °C. They are formed by two resonances at 65.5 and 3.73 ppm, assigned to tetra- and octahedral Al coordination, respectively. The Al with pentahedral coordination is absent in all samples, implying the inhomogeneity of colloidal gel calcined at 700 °C as compared to polymeric gels. The relatively stronger resonance at 65.5 ppm indicates the existence of a definite amount of $[AlO_4]$ units in gels. This is far more likely due to two causes: one is the formation of $\gamma-Al_2O_3$ and the other is the existence of inorganic networks of $-Si-O-Al-$ linkages. The latter presumption is supported by the results of ^{29}Si MAS–NMR, where a partial

amount of Al and Si atoms has been shown to mix in atomic scale at 700 °C.

The ^{27}Al MAS–NMR spectra of M60 gels calcined at different temperatures are given in Fig. 8. With increasing temperature, a new resonance at 43 ppm appears, assignable to tetrahedral coordinated Al. At 1300 °C, a certain amount of mullite has formed, as indicated by the three resonance at 63, 43 and -1.4 ppm. The two tetrahedral resonances at 63 and 43 ppm are much weak, while the octahedral peak at -1.4 ppm is fairly strong. This is considered to result from the co-existence of $\theta-Al_2O_3$ with mullite phase, as evidenced by XRD results. The intensities of two tetrahedral components increase with temperature, conversely, that of the octahedral one decreases due to the more combination of Al atoms with Si component.² At 1600 °C, the gel displays three resonances with almost same intensities, characteristic of mullite.⁸

In order to obtain an insight into the structural changes of aluminosilicate gel around the formation of mullite, the ^{27}Al MAS–NMR spectra of M60 sample were simulated with Gaussian function and the deconvolved curves are shown in Fig. 9. As a result, the occupancy percent of various coordinated Al sites were calculated according to the areas below the corresponding fitted peaks, as shown in Fig. 10. The distributions of tetra- and octahedral coordinated Al do not change significantly with temperature up to 1300 °C, above which they show a remarkable increase or decrease, respectively. This

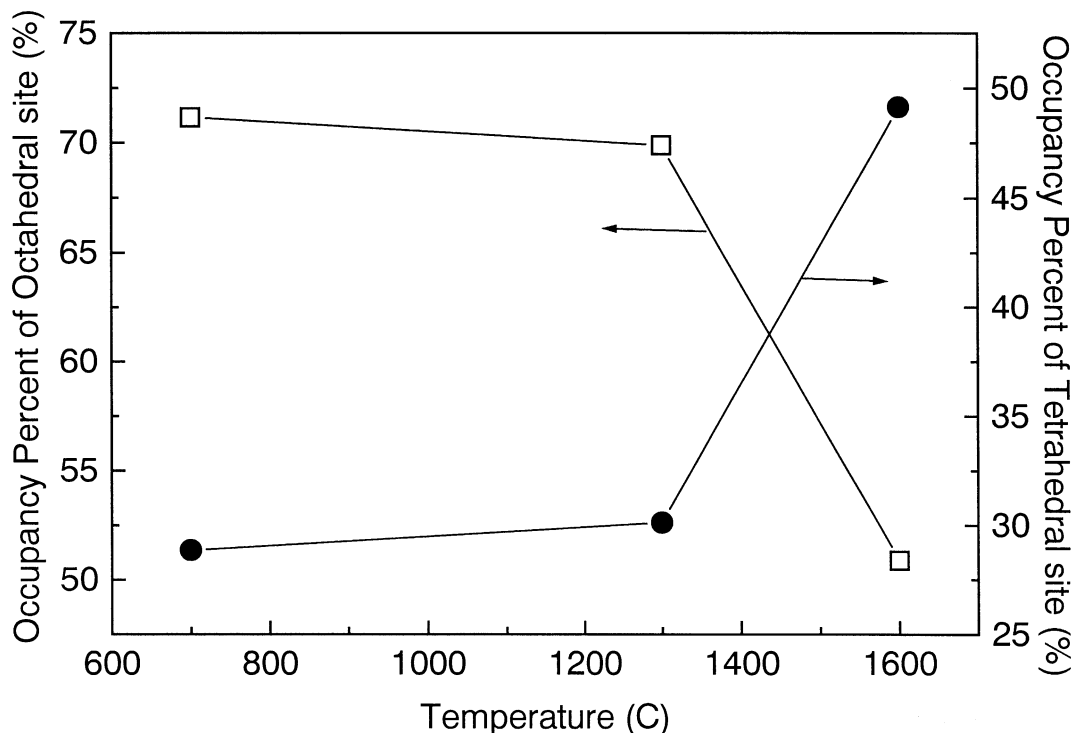


Fig. 10. Occupancy per cent of tetra- and octahedral coordinated Al in M60 gels at different temperatures.

might signify that the initially formed mullite is produced by the tetra- and octahedral Al units existing in the original precursors, no new substitution of Al for Si atom occurs in the tetrahedral units at the beginning of mullite formation. In the following process, Al atom in $[\text{AlO}_6]$ units is substituted for Si atom progressively to form $[\text{AlO}_4]$ units. The so-formed $[\text{AlO}_4]$ units will sequentially incorporate with $[\text{SiO}_4]$ and $[\text{AlO}_6]$ units, originally existing in the matrix, to produce mullite later.

The above results reveal that the synthesized mullite gel in this study is in fact a hybrid gel containing a mixture of a single-phase gel and a diphasic gel. The initially formed mullite is produced by the atoms existed in the single-phase part of the matrix. However, the mullitization behavior of the single-phase part is quite different from that of the true single-phase gel, but similar to that of true diphasic mullite gel. The mullitization of hybrid aluminosilicate gel exhibits a consecutive one-step process other than a two-stage process as reported by Li and Thomson.⁵ Therefore, it is reasonable to state that the formation behavior of mullite from hybrid gel is mainly dependent on the nature of dominant matrix part, but not on that of minor matrix part in gel.

4. Conclusions

Orthorhombic mullite directly forms from hybrid colloidal aluminosilicate gels at ca. 1300 °C, quite different from the case of polymeric aluminosilicate gels. The gel with excessive SiO_2 content compared with stoichiometric 3:2 mullite is relatively easier to form orthorhombic mullite than the others. Mullitization is a slow process in kinetics. A proper and slow heating schedule is necessary for the complete achievement of mullitization at somewhat lower temperature.

The synthesized mullite colloidal gel in this study is a hybrid gel containing a mixture of a single-phase gel and a diphasic gel. The initially formed mullite is produced by the tetra- and octahedral Al units, existing in the original precursors, i.e. in the single-phase part matrix, no new substitution of Al for Si atom occurs in the tetrahedral units at the beginning of mullite formation. Following the achievement of mullitization from

the single-phase part, Al atom in $[\text{AlO}_6]$ units is substituted for Si atom progressively to form $[\text{AlO}_4]$ units. The so-formed $[\text{AlO}_4]$ units then incorporate with $[\text{SiO}_4]$ and $[\text{AlO}_6]$ units existing originally in the diphasic part, to produce mullite. The mullitization behavior of hybrid aluminosilicate gel mainly depends on the nature of dominant matrix part, but not on that of minor matrix part in gel. During the formation process of mullite, amorphous Si-rich phase appears as a transitional phase, which may be not detectable in XRD analysis.

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References

1. Al-Jarsha, Y. M. M., Biddle, K. D. and Das, A. K. *et al.*, Mullite formation from ethyl silicate and aluminum chlorides. *J. Mater. Sci.*, 1985, **20**, 1773–1781.
2. Sanz, J., Sobrados, I. and Cavalieri, A. L. *et al.*, Structural changes induced on mullite precursors by thermal treatment: ^{27}Al MAS-NMR investigation. *J. Am. Ceram. Soc.*, 1991, **74**(10), 2398–2403.
3. Li, D. X. and Thomson, W. J., Mullite formation from non-stoichiometric diphasic precursors. *J. Am. Ceram. Soc.*, 1991, **74**(10), 2382–2387.
4. Yoldas, B. E. and Partlow, D. P., Formation of mullite and other alumina-based ceramics via hydrolytic polycondensation of alkoxides and resultant ultra- and micro-structural effects. *J. Mater. Sci.*, 1988, **23**, 1895.
5. Li, D. X. and Thomson, W. J., Effects of hydrolysis on the kinetics of high-temperature transformations in aluminosilicate gels. *J. Am. Ceram. Soc.*, 1991, **74**(3), 574–578.
6. Aksay, I. A. and Pask, J. A., Stable and meta-stable equilibria in the system $\text{SiO}_2\text{-Al}_2\text{O}_3$. *J. Am. Ceram. Soc.*, 1975, **58**(11-12), 507–512.
7. Tkalcec, E., Hoebbel, D. and Nass, R. *et al.*, Structural changes of mullite precursors in presence of polyethyleneimine. *J. Non-Cryst. Solids*, 1999, **243**, 233–243.
8. Selvaraj, U., Komarneni, S. and Roy, R., Structural differences in mullite xerogels from different precursors characterized by ^{27}Al and ^{29}Si MAS NMR. *J. Solid State Chem.*, 1993, **106**, 73–82.