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Formation of Mullite and Spinel Phases from $SiO_2-Al_2O_3$ Gels Prepared by a Spray Pyrolysis Technique. A ^{29}Si and ^{27}Al MAS NMR Study

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Thermal behavior of alumino-silicate gels prepared by spray pyrolysis, with Al/Si ratios between 1.5 and 18, has been analyzed by differential thermal analysis (DTA), X-ray diffraction, transmission electron microscopy, IR, and ^{29}Si and ^{27}Al magic angle spinning NMR techniques. In samples heated at 800 °C, tetra-, penta-, and octahedral aluminum were detected. In samples heated at 900 °C, Al-rich mullite (Al/Si = 4−6) or Si-spinel nuclei (Al/Si = 10−18) are formed after the partial segregation of SiO_2 from alumino-silicate gels. The strong rearrangement of aluminum atoms, with formation of tetra- and octahedral Al at the expense of pentahedral Al, is responsible for the exothermic peak detected at ∼980 °C in DTA curves. Thermal treatments between 1000 and 1300 °C produce the progressive incorporation of SiO_2 into newly formed mullite nuclei. In Al-rich samples, with nominal Al/Si ratios between 8 and 18, the formation of mullite nuclei is only detected above 1100 °C. In this case, spinel and mullite phases coexist in the temperature range 1100−1250 °C.

Introduction

The outstanding thermal properties of mullite and mullite−matrix composites explain the extensive interest on mullite ceramics.[1] On the other hand, mullite materials display high resistance against chemical attack (especially under oxidizing conditions), low thermal expansion coefficients, very low thermal conductivity, and excellent creep resistance that justify the use of these materials in a broad set of technological applications.[2−4]

Mullite is the only stable phase of the $SiO_2-Al_2O_3$ binary system.[5,6] The structure of mullite is formed by edge-shared AlO_6 octahedral chains parallel to the *c*-axis that are interconnected by double chains of TO_4 ($T = Si^{4+}$ or Al^{3+}) tetrahedra[7−12] (Figure 1). The structural formula of mullite is given by the expression $Al^{VI}_2(Al^{IV}_{2+2x}Si_{2-2x})O_{10-x}$ where x ranges between 0.17 and 0.57. Cameron found a linear relation between the length of the *a*-axis and the mullite composition.[13] Mullites formed at 980 °C from synthetic or mineral precursors are rich in alumina; however, a progressive contraction of the unit cell of mullite is observed when SiO_2 is incorporated into the mullite at increasing temperatures.[6,13]

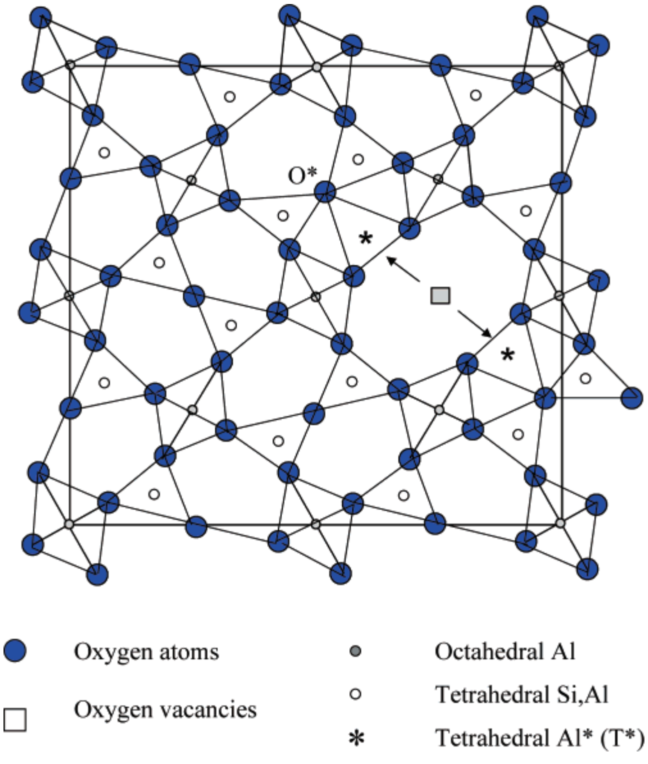

Figure 1. Projection of the mullite structure along the *c*-axis, in which structural rearrangements produced around oxygen vacancies are illustrated.

To this day, the formation mechanism of mullite from alumino-silicates remains unclear. Formation of mullite from kaolinite is produced at 980 °C; however, mullite can only

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be obtained from pyrophyllite at 1250 °C.[14−19] On the other hand, sol−gel and coprecipitation techniques allow the preparation of homogeneous pure materials at the nanometric scale.[20−23] Yoldas and Partlow examined the effect of preparation conditions and precursors used in the synthesis of monophasic gels.[22] In alumino-silicate gels, the formation of mullite or spinel at 980°C depends mainly on the composition and chemical homogeneity of precursors. Formation of mullite at 980 °C is also favored in $SiO_2-Al_2O_3$ gels prepared by spray pyrolysis. With this technique, the preparation of homogeneous particles with a fixed composition can be achieved in a single step.[24]

NMR spectroscopy is a very useful technique to analyze the chemical environment of atoms.[25] The analysis of structural changes produced during thermal treatments of amorphous $SiO_2 \cdot Al_2O_3$ gels confers on this technique the possibility of studying the mullite formation.[23,26,27] In previous works, NMR spectroscopy showed that elimination of pentahedral Al is responsible for the exothermic peak detected at 980 °C in DTA curves of synthetic gels or natural precursors.[6,15,27] In this process, the segregation of SiO_2 from aluminosilicate gels favored the formation of Al-rich mullite and/or spinel nuclei; however, the conditions required for the formation of the two phases were not well established.[6,23,26,27]

In this work, we have investigated structural changes produced during the calcination of monophasic $SiO_2 \cdot Al_2O_3$ gels prepared by spray pyrolysis. For that, ^{29}Si and ^{27}Al magic angle spinning (MAS) NMR techniques have been used to monitor cation environments and polyhedra condensation in samples heated at increasing temperatures. The preparation of alumino-silicates with different compositions has permitted the compositional range of spinels and mullites to be determined. In this work, special attention has been paid to study the incorporation of Si into mullite precursors.

Experimental Section

Samples Preparation. Starting solutions were prepared by dissolving hydrated aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, and tetraethoxysilane (TEOS), $C_8O_{20}H_4Si$, in methanol. The 0.1 mol/L solutions with Al/Si ratios of 1.5, 2.3, 3, 4, 4.7, 8, and 18 were used to prepare the M15, M23, M30, M40, M47, M80, and M180 samples.

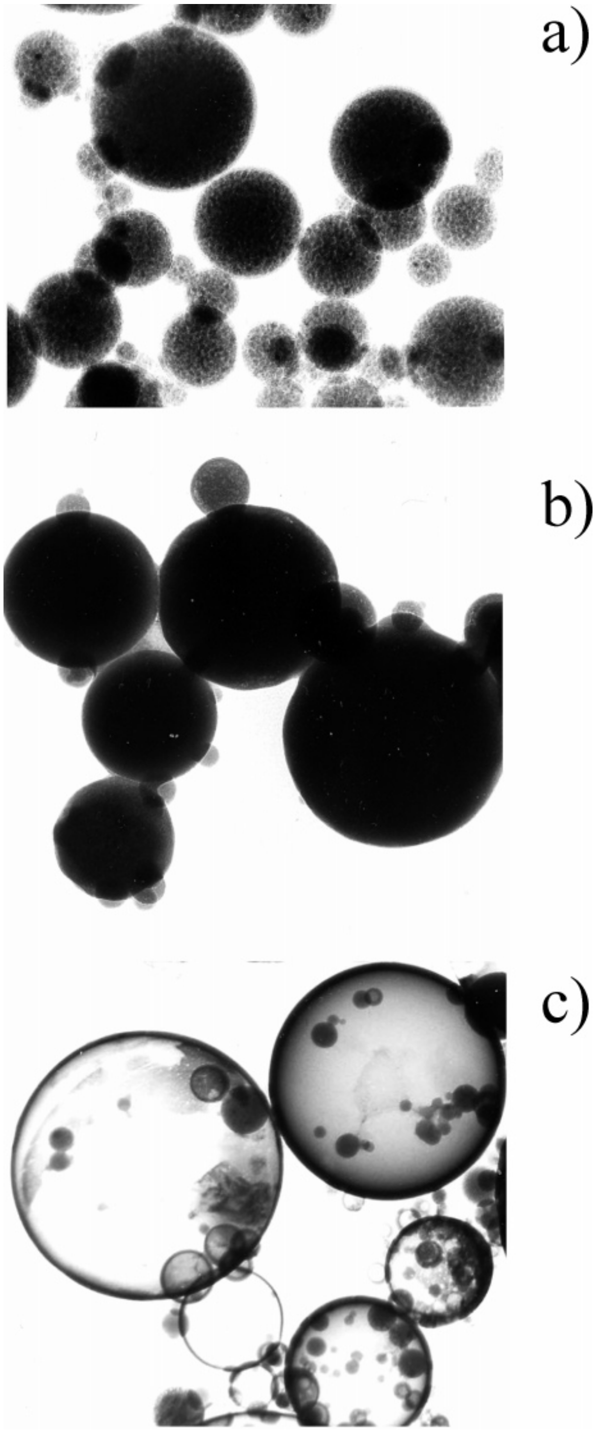

Figure 2. TEM micrographs illustrating the influence of the furnace temperature on morphology and mean size of particles prepared by spray pyrolysis at (a) 500 °C, (b) 550 °C, and (c) 800 °C.

Solutions were sprayed with compressed air at a constant flow rate of 1.60 mL/min, with a pressure of $1.8.10^2$ kPa, through a nozzle atomizer with a moving needle, designed to control the particle size of droplets in spray pyrolysis preparations. Experimental conditions were chosen to produce dense, fine, non-agglomerated mullite powders with a controlled spherical particle size distribution (see Figure 2). The gas was made to enter a low-temperature furnace (250 °C), where the solvent was evaporated. Then, the spray enters a second furnace kept at 550 °C, where the decomposition of salts produces microporous sintered particles that are finally collected.[28] In our work, droplets are near 1 μm size, and the diameters of individual particles are between 2 and 10 nm.

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Prepared samples were heated for 2 h in air at increasing temperatures between 600 and 1300 °C. After each treatment, the samples were analyzed with IR, NMR, transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques to analyze structural transformations produced.

Techniques. Differential thermal analysis (DTA) experiments were carried out up to 1300 °C in static air using a Stanton Redcroft-780 instrument with Pt−Pt/Rh 13% thermocouples. The heating rate used was 12 °C/min. Alumina calcined at 1400 °C was used as a reference.

The identification of formed phases was carried out with the XRD technique. XRD patterns were recorded in a Philips X'pert diffractometer working at 28 mA and 36 kV, with a Ge(111) monochromatized Cu Kα_1 radiation ($\lambda = 1.5405981$ Å). Data were taken between 5 and 80° with a scanning rate of 1° (2θ)/min.

The morphology and dispersion of particles were studied by means of TEM in a Philips 300 apparatus. In this study, the samples were ultrasonically dispersed in water and transferred to carbon-coated copper grids. The TEM study indicated that particles are nonhollow and nonagglomerate. Mean-particle sizes were calculated from the analysis of ten micrographs recorded on samples calcined at 600 °C. The analysis of powder size distributions gave mean diameters (d_m) near 0.50 μm with standard deviations (σ) ~ 0.7.

Samples were diluted with KBr to form pellets (sample/KBr = 5% by weight) and examined by IR spectrometry in the 240−4000 cm^{-1} region, using a Nicolet 20 SXC FT-IR spectrophotometer. A high purity polystyrene foil was used to calibrate the instrument; errors in band positions were estimated lower than 2 cm^{-1}.

High resolution ^{29}Si ($I = 1/2$) and ^{27}Al ($I = 5/2$) MAS NMR spectra of powdered samples were recorded at room temperature in an Avance 400 Bruker spectrometer, equipped with a Fourier transform unit. Resonance frequencies used for Si and Al were respectively 79.49 and 104.26 MHz (external magnetic field of 9.4 T). Spinning frequencies were 4 kHz for Si and 10 kHz for Al. NMR spectra were recorded after irradiation of the sample with single pulses. In the ^{29}Si NMR signal, $\pi/2$ pulses of 5 μs were used; however, in the ^{27}Al NMR signal, $\pi/8$ pulses of 2 μs were chosen for quantitative determinations. To avoid saturation effects, recycling times between 2 and 20 s were used between successive accumulations. Tetramethylsilane and 1 M $AlCl_3$ solution were used as external standard references. The mean error on chemical shift values was 0.5 ppm. Accumulations amounted to 500 and 200 free induction decays (FIDs) in Si and Al NMR signals.

The quantitative analysis of MAS NMR spectra was carried out by using the WINFIT (Bruker) software package. For spectra deconvolution, a standard nonlinear least-squares iterative method was used. The spinning rate, position, line width, and intensity of components were first determined. Quadrupole C_Q and η constants are adjustable parameters that must be determined from experimental profiles by trial and error procedures. In the quantitative analysis of spectra, relative intensities of individual components were determined by numerical integration. In the case of the Al signal, quantitative analyses were done following the procedure proposed by Massiot el al., in which second-order quadrupolar effects were considered in the analysis of central components.[29] In this analysis, the contribution of spinning sidebands ascribed to ±(1/2, 3/2) and ±(3/2, 5/2) transitions were subtracted from the central (−1/2, 1/2) transition. In some cases, the asymmetry of octahedral Al components was taken into consideration by incorporating a second component in spectra deconvolutions. Errors in determination of relative band intensities were estimated as lower than 5%.

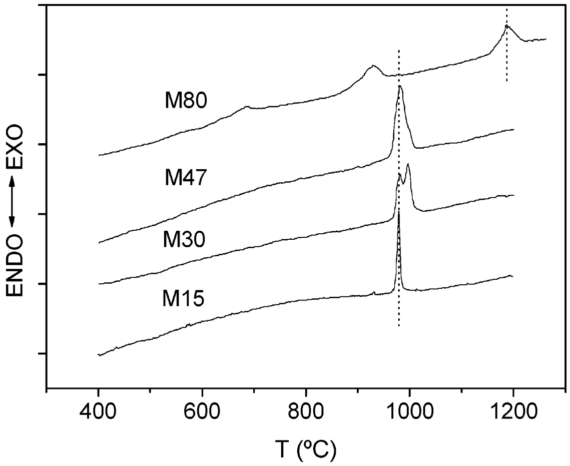

Figure 3. DTA curves of samples M15, M30, M47, and M80 prepared by spray pyrolysis. In Si rich samples, the exothermic peak at 980°C is associated with formation of mullite. In Al-rich samples, exothermic peaks at 980 and 1230 °C have been ascribed to formation of spinel and mullite phases.

Results

DTA Results. DTA curves of gels prepared by spray pyrolysis are given in Figure 3. In samples with Al/Si between 1.5 and 4.7, the detection of small endothermic peaks near 500 °C has been ascribed to the partial dehydroxylation of precursors and the detection of exothermic peaks between 950 and 1000 °C to formation of mullite nuclei. In samples with Al/Si = 8 and 18, the peak detected at 930 °C has been assigned to the formation of the spinel phase and the peak at 1230 °C has been assigned to the formation of mullite.[6,27] In these samples, the formation of mullite is delayed to higher temperatures by the formation of the spinel phase.

XRD Results. XRD patterns of four representative samples, Al/Si = 1.5, 3, 4.7, and 8, heated between 800 and 1200 °C, are given in Figure 4. In all cases, the XRD patterns of samples heated at 800 °C correspond to amorphous samples. In Si-rich samples, a broad band ascribed to amorphous SiO_2 was detected at $2\theta \sim 25°$.[6,27] In samples Al/Si = 3 and 4.7, besides the SiO_2 peak, small narrow peaks of mullite were detected. In Al-rich samples, besides the SiO_2 peak at 25°, small broad bands of the γ-Al_2O_3 phase were detected at 33, 38, 47, 62, and 67°.[6,27]

Strong modifications were detected in XRD patterns of samples heated at 900 °C. In the case of samples with Al/Si = 1.5 and 8 (Si- and Al-rich phases), the intensity of mullite peaks is small; however, in samples with Al/Si = 3 and 4.7, the amount of mullite is considerable. The intensity of mullite or spinel peaks increases at 1000 and 1100 °C. In samples heated at 1200 °C, the amount of formed mullite is always important; however, the broad peaks of the starting gels still remain, indicating that the amount of amorphous phases is still considerable and requires higher temperatures for its complete elimination.

IR Spectroscopy. IR spectra (400−1500 cm^{-1} region) of the analyzed samples are given in Figure 5. In all cases, the

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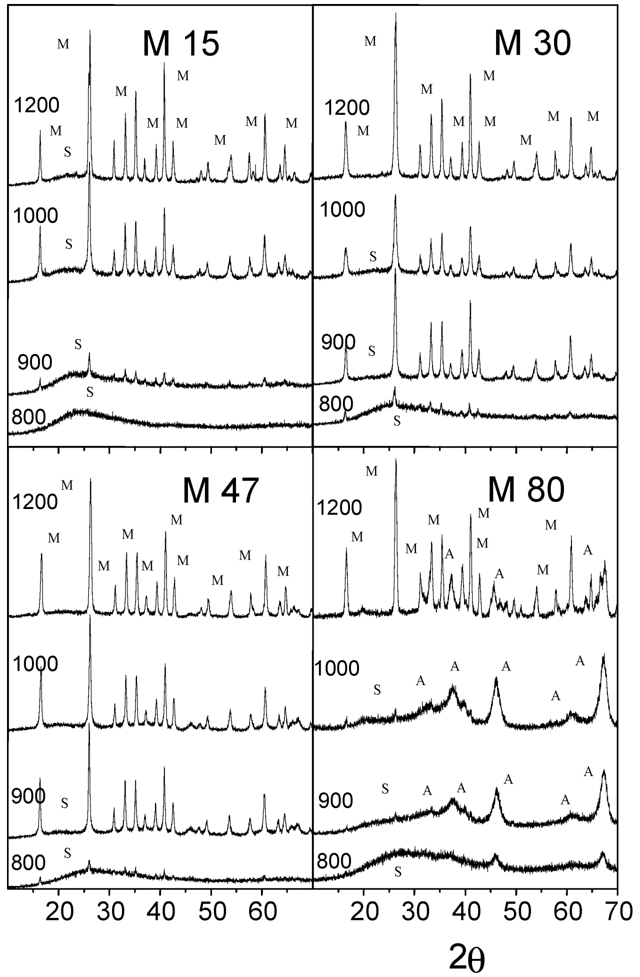

Figure 4. Temperature dependence of XRD patterns of samples M15, M30, M47, and M80 prepared by spray pyrolysis. Diffraction peaks of silica, mullite, and alumina are denoted with S, M, and A symbols.

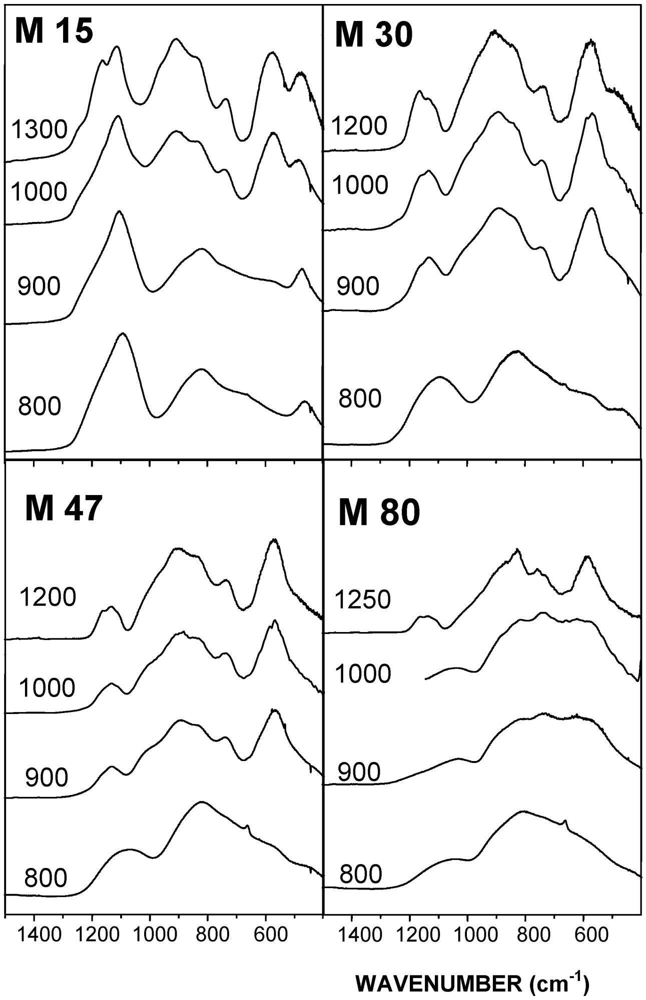

Figure 5. IR spectra of samples M15, M30, M47, and M80 heated between 800 and 1300 °C.

IR spectra of samples heated at 800 °C are formed by four components at 1100, 830, 600, and 480 cm^{-1}. Bands at 1100 and 480 cm^{-1} are ascribed to stretching and bending modes of SiO_4 tetrahedra, but those at 830 and 600 cm^{-1} correspond to different coordinations of Al. In samples heated at 1200 °C, mullite formation increases considerably the intensity of the bands centered at 600 and 900 cm^{-1}, ascribed to the formation of octa- and tetrahedrally coordinated Al.[30,31] In samples with stoichiometry near that of mullite, IR spectra of samples heated at 900 °C already display the spectral features of this phase. Formation of mullite favors also the detection of a doublet at 1150 and a band at 750 cm^{-1}.

NMR Spectroscopy. ^{27}Al (I = 5/2) and ^{29}Si (I = 1/2) MAS NMR spectra of samples heated between 800 and 1300 °C are given in Figures 6−8.

^{27}Al MAS NMR. ^{27}Al MAS NMR spectra of samples heated at 800 °C display three components at ~60, 30, and 0 ppm that are due to aluminum in tetra-, penta-, and octahedral coordination.[25] In general, the intensity of pentahedral Al is more important than those of tetra- and octahedral Al; however, in the case of samples with Al/Si = 3 and 4.7 the amount of tetra- and octahedral Al increases, and in samples with Al/Si = 8 and 18, the amount of octahedral Al is higher than those of two other coordinations.

The local structure of gels changes considerably when alumino-silicate gels are heated at 900 °C. In all cases, tetra- and octahedral Al increase at the expense of pentahedral Al. The amount of tetrahedral Al changes also with sample composition: in Al-rich samples, tetrahedral Al is lower than octahedral Al; however, in Si-rich samples the intensity of tetrahedral Al components becomes higher than that of octahedral Al.

In most samples heated between 1000 and 1300 °C, two tetrahedral components were detected at 42 and 60 ppm in ^{27}Al MAS NMR spectra. The intensity of tetrahedral components increases with temperature, reaching at 1200 °C the typical NMR spectrum of mullite 3:2 (samples M15 and M30). In aluminosilicate gels with Al/Si = 8 and 18, tetrahedral components appear when mullite nuclei are detected in XRD patterns.

In deconvolution of ^{27}Al MAS NMR spectra of starting gels, the observed spinning sidebands correspond to those of the central (−1/2, 1/2) and the satellite (−1/2, −3/2) and (1/2, 3/2) transitions. In mullites, ^{27}Al MAS NMR spectra are formed by the central (−1/2, 1/2) and satellite (−3/2, −5/2), (−1/2, −3/2), (1/2, 3/2), and (3/2, 5/2) transitions. The analysis of experimental envelopes has allowed quad-

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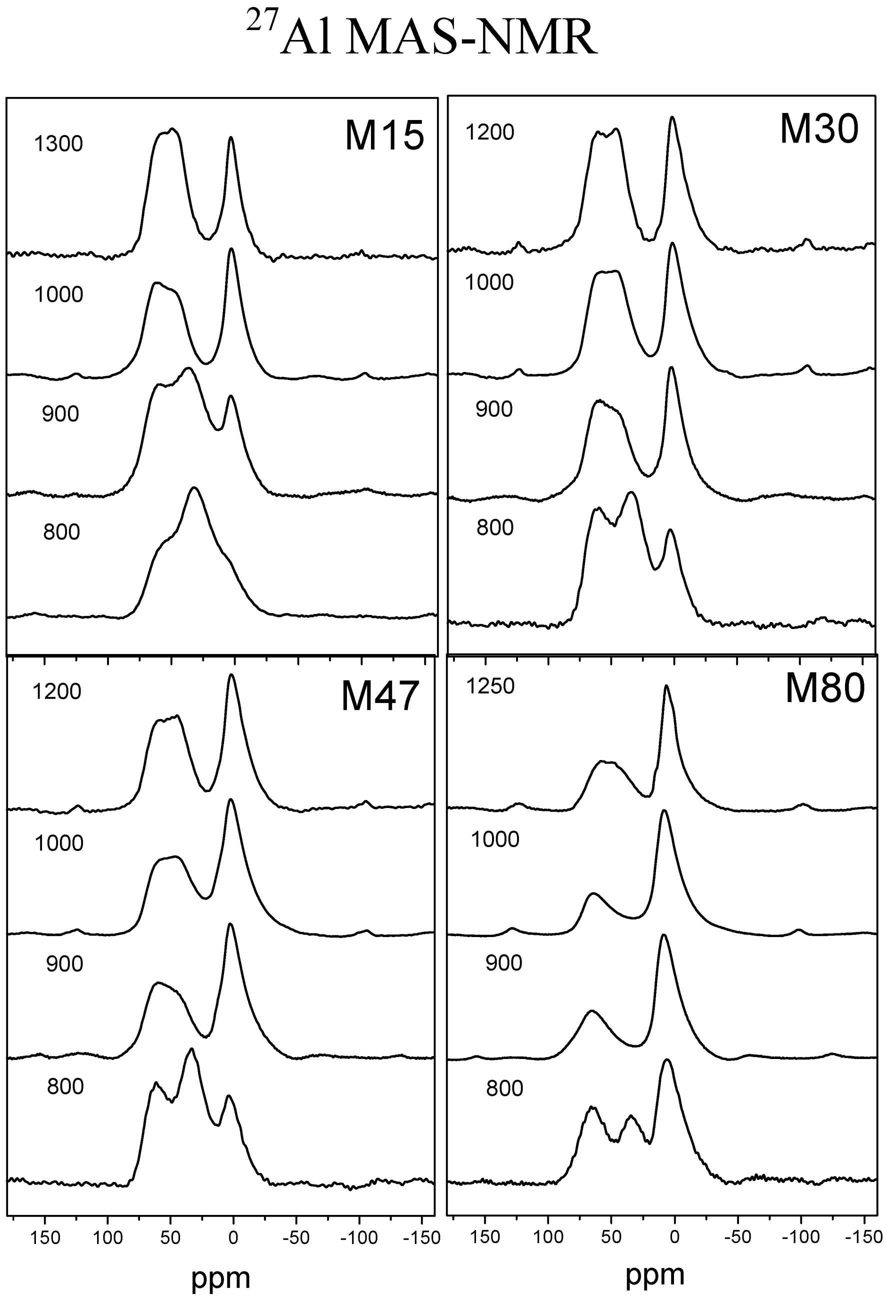

Figure 6. ^{27}Al MAS NMR spectra of samples M15, M30, M47, and M80, heated between 800 and 1300 °C. The three resolved bands correspond to tetra-, penta-, and octahedral coordinations of aluminum.

rupole interactions to be estimated and the contribution of spinning sidebands of lateral transitions to central components to be determined (see Figure 7). Relative amounts of tetra-, penta-, and octahedral Al deduced from central ^{27}Al MAS NMR components are given in Table 1 in Supporting Information (see Al_T, Al_P, and Al_O values).

^{29}Si MAS NMR. ^{29}Si MAS NMR spectra of samples heated at 800 °C display a broad component that shifts toward more positive values as the Al content increases (see Figure 8). The deconvolution of ^{29}Si MAS NMR spectra showed the presence of two bands at −100 and −85 ppm, whose relative intensities change with composition.

In samples heated at 900 °C, important changes are detected in ^{29}Si NMR spectra. In all cases, the two components detected near −89 and −110 ppm have been ascribed to Si in amorphous aluminosilicates and SiO_2 phases. The intensity of the −110 ppm band increases considerably with the SiO_2 content. In most analyzed samples, the intensity of the −110 ppm component decreases when mullite is formed and almost disappears at 1200 °C. Only in the sample Al/Si = 1.5 (Si rich gel), the intensity of this band remains appreciable at 1200 °C.

In all samples, the broad component detected at −89 ppm decreases progressively when the calcination temperature increases; however, the complete elimination of this band requires higher temperatures than those used in this work. In all analyzed samples, four narrow components are detected at −82.5, −87, −90.5, and −94.5 ppm when mullite is detected in XRD patterns. The intensities of these components change with temperature and composition of the samples. In general, the intensities of the −82.5 and −90.5 ppm components decrease with calcination temperature, but

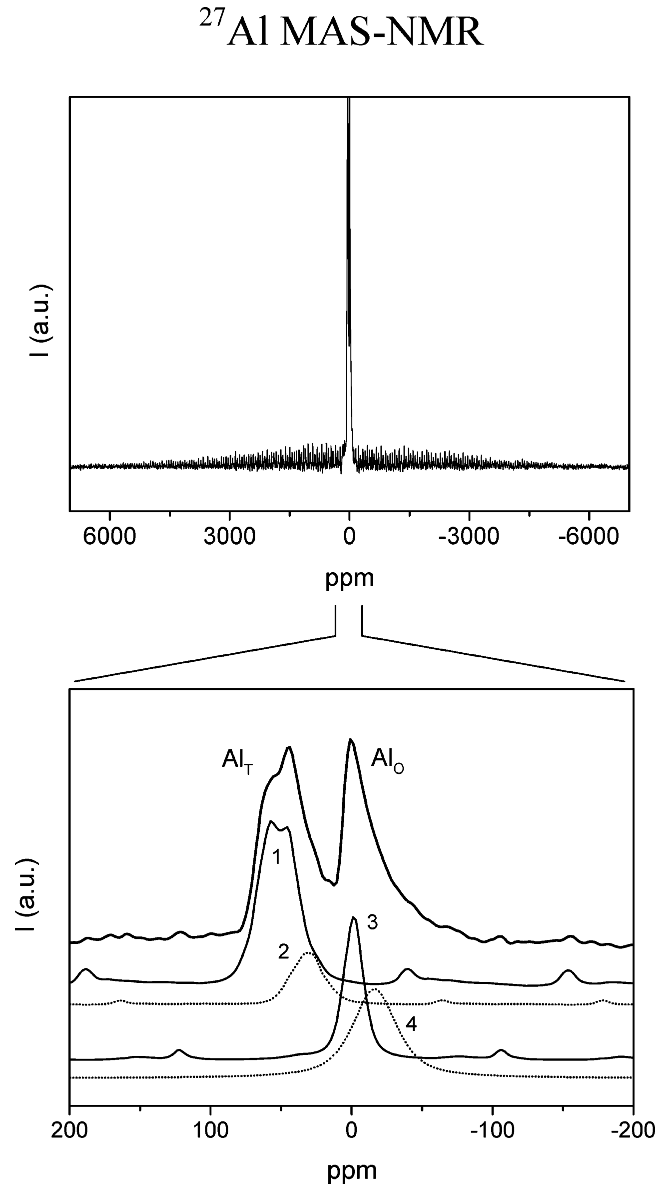

Figure 7. ^{27}Al MAS NMR spectra of the sample M30 heated at 1200 °C. In deconvolution of the experimental profiles, two tetrahedral (1 and 2) and two octahedral (3 and 4) components have been used (bottom). In simulation of the central (−1/2, 1/2) transition, second-order quadrupolar effects have been considered. Relative intensities of components have been deduced by numerical integration (see text).

that of the −82.5 ppm peak decreases also with Si content. In the case of the sample Al/Si = 1.5 heated at 1200 °C, only the component at −87 ppm displays high intensity.

In deconvolution of ^{29}Si MAS NMR spectra of samples, four components ascribed to mullite, one to silica and one to the aluminosilicate gel, have been considered. Information deduced from the quantitative analysis of ^{29}Si MAS NMR spectra is given in Table 1 (see Supporting Information). In this Table, the relative amounts of Si in mullite, aluminosilicate gel (AlSigel), and silica are given.

Discussion

The structural formula of mullites is given by the expression $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$ where x ranges between 0.17 and 0.57. The structure of mullite derives from that of the sillimanite ($x = 0$) by replacement of Si by Al, according to the substitutional scheme[13]

$$O^{2-} + 2Si^{4+} \rightarrow \square + 2Al^{3+}$$

where □ stands for oxygen vacancies. The mullite 3:2 ($3Al_2O_3{\cdot}2SiO_2$) corresponds to $x = 0.25$, and the mullite 2:1 ($2Al_2O_3{\cdot}SiO_2$) corresponds to $x = 0.40$.

The stucture of mullite is formed by edge-shared AlO_6 octahedral chains parallel to the *c*-axis that are interconnected by double chains of TO_4 (T = Si^{4+} or Al^{3+}) tetrahedra (Figure 1). Oxygen vacancies created by substitution of Si by Al are located at the common corner of two tetrahedra (sites O_3). To maintain the fourfold coordination, tetrahedral cations near oxygen vacancies are shifted to new tetrahedral sites designed T*. In this case, oxygen atoms shift toward T* sites and coordinate three tetrahedral cations (sites O*).

The formation of mullite is produced at 980 °C in kaolinites, but only at 1250 °C in pyrophyllite.[14−19] In both cases the formation of mullite was produced when tetrahedral layers were broken, and Si and Al atoms can rearrange in a different way. The formation of mullite has also been extensively studied in aluminosilicate gels prepared with sol−gel and coprecipitation techniques. In diphasic gels formation of mullite is produced at 1250 °C, but in monophasic gels mullite is detected at 980 °C.[6,20−23,27,32,33] At present, it is assumed that the formation of mullite at 980 °C depends on the precursor homogeneity. When the segregation of SiO_2 and Al_2O_3 is produced, the formation of mullite can be delayed to temperatures near 1250 °C.[6,23,27] On the other hand, formation of mullite at 980 °C is favored in $3Al_2O_3{\cdot}2SiO_2$ gels prepared by spray pyrolysis.[24,27]

Aluminosilicate Gels Prepared by Spray Pyrolysis. In aluminosilicate gels prepared by spray pyrolysis, the ^{27}Al MAS NMR spectra of samples heated at 800 °C are formed by three broad components ascribed to tetra-, penta-, and octahedrally coordinated aluminum and their corresponding sidebands. The analysis of ^{27}Al MAS NMR spectra showed that quadrupolar interactions associated with Al sites display ν_Q values near 1 MHz. The existence of a big heterogeneity on Al environments widens considerably the spinning sidebands of lateral (−1/2, −3/2) and (1/2, 3/2) transitions, impeding the precise determination of quadrupolar parameters.[34]

The analysis of prepared gels showed that the intensity of the pentahedral Al is more important than those of the tetra- and octahedral Al bands in samples with Al/Si between 1.5 and 4.7. In samples with Al/Si = 8 and 18, the amount of octahedral Al is bigger than that of tetra- and pentahedral Al (see Figure 6). On the basis of these results, it has been concluded that the local arrangement of aluminum is different in Si- and Al-rich samples. In the first case, the presence of Si favors the metastable pentahedral coordination of Al; in the second case the small amount of Si incorporated does

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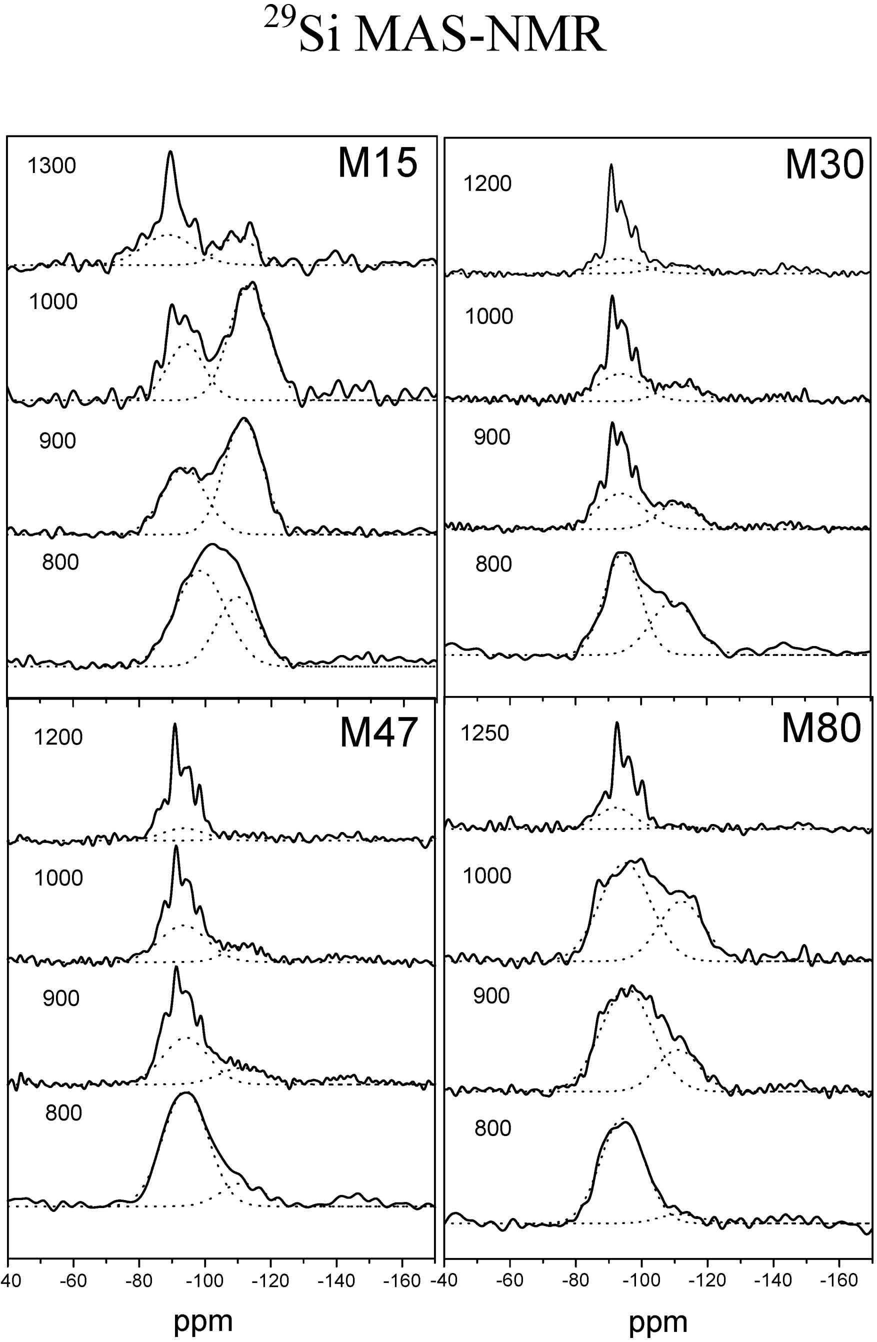

Figure 8. ^{29}Si MAS NMR spectra of samples M15, M30, M47, and M80 heated between 800 and 1300 °C. In these spectra, narrow components correspond to the mullite, and broad bands correspond to amorphous silica and aluminosilicate phases.

not affect the arrangement of Al adopted by transitional aluminas.[6,35]

SiO_2 Segregation. In amorphous alumino-silicate gels heated at 900 °C, strong modifications are produced. In most samples, the detection of a band centered at -110 ppm in ^{29}Si MAS NMR spectra has been ascribed to the segregation of silica from starting gels. Moreover, tetra- and octahedral Al bands increase at the expense of the pentahedral one in ^{27}Al MAS NMR spectra. Similar results have been reported previously in aluminosilicate gels, which were ascribed to the formation of mullite nuclei.[6,23,27,32] However, other authors have proved that the exothermic peak at 980 °C is mainly due to the formation of tetra- and octahedral Al at the expense of pentahedral Al during SiO_2 segregation.[6,27]

The amount of segregated SiO_2 is maximum in samples heated at 900 °C and decreases as the nominal Al content increases (Figure 9). In Al rich samples (with Al/Si = 8 and 18), the segregation of SiO_2 was also observed at 1100 °C, when mullite nuclei are detected in XRD patterns. In this work, the chemical composition of the remaining aluminosilicates has been analyzed. To that end, the deconvolution of ^{29}Si MAS NMR spectra was performed, and relative intensities of the components at -89 and -110 ppm were calculated. The amount of segregated silica was finally subtracted from nominal compositions to calculate the composition of aluminosilicate gels. In Figure 10, the

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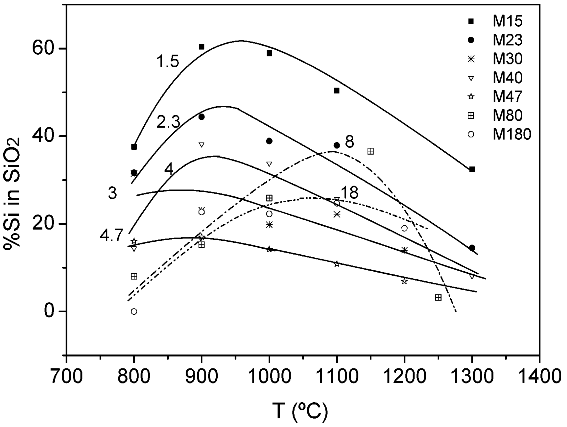

Figure 9. Amount of SiO_2 segregated in samples heated at increasing temperatures, as deduced from ^{29}Si MAS NMR spectra.

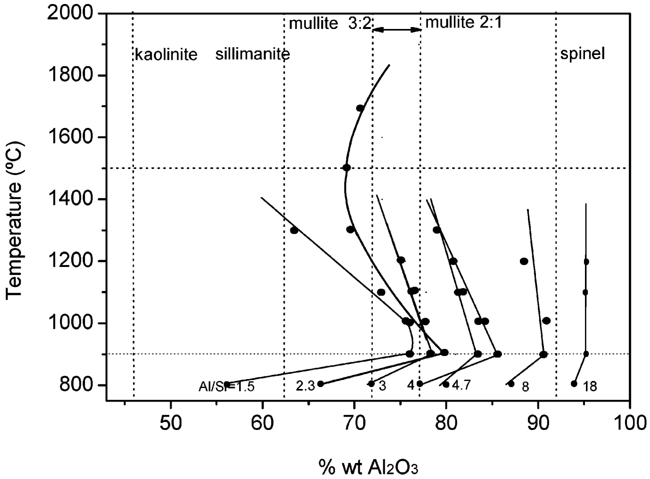

Figure 10. Temperature dependence of aluminosilicates composition (expressed as Al/Si ratio). The plotted values were deduced after subtraction of segregated silica from nominal compositions. In this figure, compositions of kaolinite, sillimanite, mullites 2:1 and 3:2, and spinel are indicated in wt % Al_2O_3.

composition of remaining aluminosilicates is analyzed as a function of the calcination temperature. Variations produced on the composition of Si-rich samples are higher than those produced in Al-rich samples.

Samples with nominal Al/Si ratios between 1.5 and 4.7 display at 1000 °C the characteristic ^{27}Al NMR spectrum of mullites.[23,27,36−41] In these samples, two tetrahedral components at 66 and 40 ppm were detected besides the octahedral component at ~0 ppm. On the other hand, samples with Al/Si between 8 and 18 display specific features of transitional aluminas.[35] In this case, the tetrahedral component at 60 ppm displays a lower intensity than that of octahedral Al. At this point, it is important to remark that Al/Si ratios estimated for aluminosilicate gels with structural features of mullite, comprised between 4 and 7, are clearly higher than those found in more stable mullites (Al/Si ~ 2.9−3.5).[6,13] This observation is parallel with results reported in other works, where Al-rich mullites were detected in aluminosilicate gels heated at 980 °C.[6,23,27,41] In samples with nominal Al/Si ratios of 8 and 18, the aluminosilicates formed display Al/Si values similar to those of the starting gels (Figure 10).

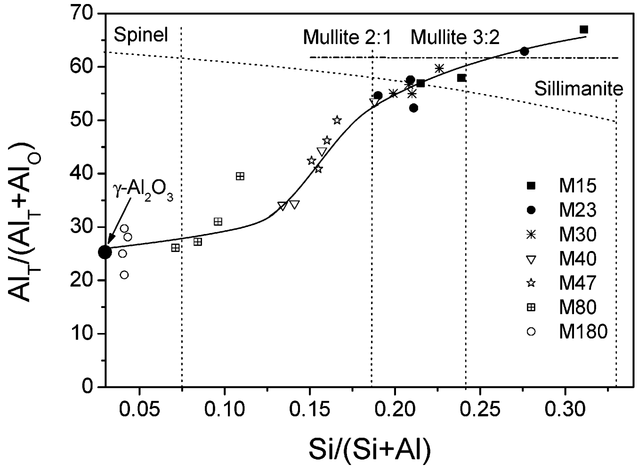

Figure 11. Influence of the Si content on the amount of tetrahedral Al detected in the analyzed samples. The tetrahedral Al contents deduced from the mullites formula are included as a dotted line.

In samples heated between 1000 and 1300 °C, part of the segregated SiO_2 is incorporated into aluminosilicates, producing the increment of tetrahedral aluminum in ^{27}Al MAS NMR spectra[36] (see Figures 6 and 11). However, the observed dependence of tetrahedral Al components (bands 1 and 2) on the amount of Si differs from that expected in mullites, where incorporation of Si should produce the decrease of tetrahedral Al (see dotted line of Figure 11). On the basis of this analysis, we must conclude that the local structure of aluminosilicates formed after segregation of silica differs considerably from that of well-crystallized mullites. In Al-rich aluminosilicates, the amount of incorporated Si is considerably lower than in Si-rich aluminosilicates. In samples with Si/(Si + Al) ~ 0.15, the tetrahedral Al increase rapidly, from the values reported in spinels to those of mullites.[6,35]

Mullite Precursors. In Si-rich samples, ^{29}Si MAS NMR spectra of samples heated above 900 °C display the four narrow bands ascribed to mullite 3:2. However, in Al-rich samples, ^{29}Si MAS NMR spectra display a broad band at −89 ppm that has been ascribed to Si in amorphous aluminosilicates. The incorporation of a small amount of Si in this aluminosilicate (below 12%) favors the formation of spinels, and the incorporation of a bigger amount of Si (above 17%) favors the formation of mullite nuclei (see Figure 11). In all cases, the amount of Si incorporated in both phases depends on the amount and availability of silicon.

In samples analyzed in this work, incorporation of Si causes the simultaneous increment of the two tetrahedral Al components of the mullite, suggesting that mullite nuclei always display similar characteristics (see Figure 6). In parallel to this observation, a similar pattern formed by four narrow components at −82.5, −87, −90.5, and −94.5 ppm is detected in the Si MAS NMR spectra of samples heated between 1000 and 1300 °C (Figure 8).

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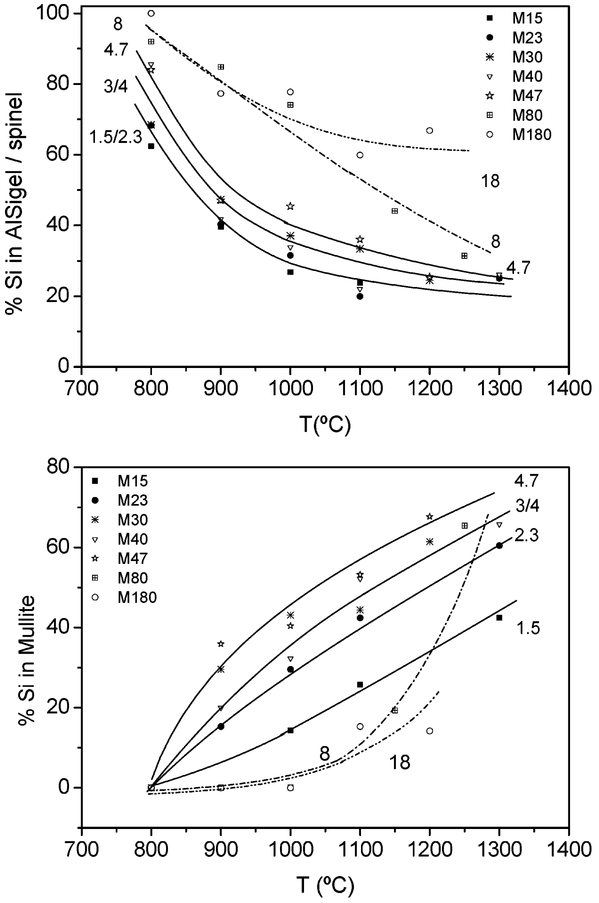

Figure 12. Amount of Si in mullites (a) and in AlSi gels/spinel phases (b) deduced from ^{29}Si MAS NMR spectra.

Al/Si ranges deduced for aluminosilicates formed at 1000 °C are higher than compositional limits deduced for stable mullites (2.8$-$3.5), suggesting that other phases with higher Al content could have been formed. In accordance with this idea, the broad band detected at -89 ppm in ^{29}Si MAS NMR spectra of analyzed samples has been ascribed to an Al rich amorphous aluminosilicate. To estimate the amount of silicon incorporated in mullite and the amorphous aluminosilicate, we have deconvoluted the broad band at the -89 ppm peak into five components: one broad peak ascribed to the amorphous aluminosilicate and four narrow ones associated with different environments of Si in mullites. In a previous work, the broad band was assigned to Si in specific sites of the mullite; however, line width and intensity of this component differ from those displayed by the mullite.[37] Results deduced in this analysis are given in Figure 12. In all analyzed samples, the amount of Si incorporated into the mullite increases at the expense of the segregated SiO_2. In parallel to this observation, the amount of Si ascribed to the amorphous aluminosilicate decreases progressively as the mullite is formed, suggesting that the -89 ppm band corresponds to a mullite precursor (Figure 12a). However, the amount of Si in mullite is always lower than 75%, indicating that the total elimination of the amorphous phase requires higher temperatures than used in this work (Figure 12b).

If it is assumed that the amount of silicon incorporated into the mullite is comprised between that of mullite 2:1 ($2Al_2O_3.SiO_2$) and that of mullite 3:2 ($3Al_2O_3{\cdot}2SiO_2$), the chemical composition of the amorphous aluminosilicate must change according to the starting gel composition. Only in samples with compositions near that of stable mullites will the composition of the amorphous phase be near Al/Si $\sim$ 3, favoring the total elimination of this phase during calcination treatments.

It must be noted that in samples where spinel (Al/Si $>$ 8) is formed, thermal treatments between 900 and 1100 °C produce the segregation of SiO_2 (Figures 8 and 9). In this case, the formation of mullite is only detected in samples heated above 1200 °C. Taking into account that the formation of mullite requires Al/Si ratios lower than 6, the formation of mullite from homogeneous Al-rich gels (Al/Si $>$ 8) requires the decomposition of starting gels and the accumulation of SiO_2 into mullite nuclei. According to this observation, the segregation of SiO_2 from aluminosilicate gels with Al/Si $>$ 8 must produce alumina and mullite nuclei. Formation of mullite is responsible for the DTA peak at 1230 °C. According to these results, incorporation of SiO_2 into aluminosilicate gels always produces the formation of the mullite, indicating that mullite is the only stable phase of the binary $Al_2O_3-SiO_2$ system.[5,6]

Mullite Formation. In mullites, Al can occupy two different sites in double tetrahedral chains that relate contiguous octahedral chains along the *c*-axis. In particular, Al atoms can share oxygens with adjacent tetrahedra in sites similar to those of sillimanite or in tetrahedral clusters generated around O* oxygens of the mullite (see Figure 1). In both sites, the effective aluminum charge must be different, which explains different chemical shifts of 60 and 40 ppm components in ^{27}Al MAS NMR spectra.[6,27,34,39,40]

In the case of the mullite 3:2, the analysis of experimental ^{27}Al MAS NMR profiles (lateral and central transitions) showed that the quadrupolar constants associated with two tetrahedral sites are respectively $\nu_Q{}^1 = 900$ kHz, $\eta^1 = 0.4$, and $\nu_Q{}^2 = 800$ kHz, $\eta^1 = 0.6$. In the case of the octahedral Al, the quadrupolar constants are $\nu_Q{}^3 = 550$ kHz, $\eta^3 = 0.7$. In spectra deconvolution, a second component was used to reproduce the strong asymmetry detected in octahedral components. In agreement with previous works, chemical shifts values of three components, corrected for quadrupolar effects, are near 71, 48, and 7 ppm.[34,39,40] In mullite 3:2, with the formula $Al^{VI}{}_2Al^{IV}{}_{2.5}Si_{1.5}O_{9.75}$, the amount of oxygen vacancies is 0.25 and the relative amounts of tetrahedral and octahedral Al are near 2.5:2. The Al_T/Al_O values deduced in the samples heated at 1200 °C are similar to that deduced from the structural formula (see Supporting Information). Similar results have been reported in previous works.[34,39,40]

The intensities of two tetrahedral components increase in the same way in all analyzed samples, indicating that both environments of Al are simultaneously formed in mullite nuclei. A similar conclusion was deduced from ^{29}Si MAS NMR spectra, where similar patterns with four narrow bands at -82.5, -87, -90.5, and -94.5 ppm are detected in mullites formed above 1000 °C. On the basis of these observations it can be concluded that mullite nuclei formed below 1200 °C display homogeneous characteristics. Additional experiments carried out in the sample M23 in the 1300$-$1700 °C interval showed a small decrease of Si incorporated to mullite. This observation agrees with thermodynamic determinations reported by the Navrotski group that showed that the mullite composition with the lowest enthalpy of formation has an Al/Si ratio of 3.2.[6]

To analyze cation/vacancy distribution in mullites, relative intensities of the four narrow peaks detected in the ^{29}Si MAS NMR spectra (renormalized to 100) must be analyzed as a function of the temperature. In Si-rich samples (Al/Si = 1.5 and 2.3), the component at −87 ppm displays a high intensity, suggesting that Si and Al alternate in an orderly way as in sillimanite.[41,42] In samples with increasing Al/Si values (3, 4, and 4.7), the intensities of −82.5, −90.5, and −94.5 ppm bands increase, indicating that the distribution of Si and Al becomes disordered. However, intensities of the −82.5 and −94.5 ppm bands always remain smaller than those of the −87 and -90.5 ppm bands, suggesting that the cation distribution follows a constant pattern in all analyzed samples. To analyze the Si and Al distribution, the assignment of detected bands is necessary before comparing experimental intensities to those deduced from simulated models.[41] However, this analysis is beyond the scope of the present work.

Conclusions

The thermal behavior of alumino-silicate gels prepared by spray pyrolysis, with Al/Si ratios between 1.5 and 18, has been analyzed by DTA, XRD, TEM, IR, and ^{29}Si and ^{27}Al MAS NMR techniques. In this work, local rearrangements produced during thermal treatments of prepared gels have been analyzed with IR and NMR spectroscopies, and the new crystalline phases formed have been identified with XRD techniques.

Aluminosilicate gels heated at 800 °C display aluminum in tetra-, penta-, and octahedral coordinations. However, the segregation of SiO_2 from starting gels, detected at 900 °C, favors the strong rearrangement of Si and Al atoms in the remaining aluminosilicates. The formation of tetra- and octahedral Al at the expense of the pentahedral Al is responsible for the exothermic peak detected at 980 °C in DTA curves. Al-rich mullites are formed at 900 °C in samples with nominal Al/Si ratios between 1.5 and 4.7; however, spinels are formed in samples with nominal Al/Si values between 8 and 18. In the last case, mullites can be formed at the expense of spinels above 1200 °C.

In samples heated above 1100 °C, the amount of Si incorporated into mullite precursors increases. However, differences in compositions of starting gels produces, in addition to mullite, the formation of an amorphous aluminosilicate of variable composition, which is not completely eliminated in the temperature range 800−1200 °C. In Si-rich samples, compositional differences are compensated by SiO_2 segregation; however, in Al-rich samples, these differences are compensated by Al_2O_3 formation.

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Supporting Information Available: Table of NMR intensities deduced from the ^{27}Al and ^{29}Si MAS NMR spectra of samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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