Comparative Study of Various Sol–Gel Preparations of Cordierite Using ^{27}Al and ^{29}Si Liquid- and Solid-State NMR Spectroscopy

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The influence of molecular precursors in the sol–gel synthesis of cordierite powders has been investigated. Several preparations have been studied by ^{29}Si and ^{27}Al liquid NMR to detect possible condensation reactions between precursors. The structure of the xerogels as well as their crystallization process into cordierite was characterized by ^{29}Si and ^{27}Al MAS NMR. A xerogel obtained from tetraethoxysilane, aluminum, and magnesium nitrates first crystallizes into $MgAl_2O_4$ spinel and then cordierite phases. It can be described as a silica gel network, with magnesium atoms and aluminum atoms in octahedral environment, dispersed in it. Preparations from silicon and aluminum alkoxides and magnesium acetate lead directly to μ- and then α-cordierite at 1000 °C. In these gels, formation of Si–O–Al bridges have been evidenced and seems to be the key parameter to form directly cordierite at low temperature, without crystallizing spinel. Indeed, such bonds in the dried gel are related to the presence of aluminum atoms in tetrahedral environment, such as in cordierite phases. On the contrary, if no co-condensation reactions have occurred between the two precursors, the aluminum atoms stay in octahedral symmetry, and spinel formation is favored.

I. Introduction

Cordierite ceramics ($Mg_2Al_4Si_5O_{18}$) are attractive materials for their low dielectric constant, high electrical resistivity and low thermal expansion coefficient.[1,2] However, dense ceramics are difficult to obtain using conventional methods (solid-state reactions, crystallization from glass) because of a very narrow sintering temperature range, just before its incongruent melting point.

Sol–gel techniques were considered as attractive synthetic alternatives to get pure cordierite powders at lower temperature. A large number of studies have been published, based on metallic alkoxides. They can be classified in three groups depending on the number of alkoxide precursors (Table I). Preparations with one alkoxide usually start from tetraethoxysilane (TEOS) and aluminum and magnesium salts.[3–7] It was already mentioned in 1955 by Roy et al.[3] In the preparations using two alkoxides,[8–12] an aluminum alkoxide, usually aluminum *sec*-butoxide, is added to TEOS. The magnesium precursor is still a salt. Preparations using only alkoxides have also been developed. They can use a mixture of three alkoxides[7,13–15] or an aluminum–magnesium double alkoxide, $Mg[Al(OEt)_4]_2$ together with TEOS.[16–18] The double alkoxide can also be generated in situ by reacting metallic magnesium with an aluminum alkoxide.[19–21]

All these preparations lead to formation of α-cordierite, but crystallization temperatures strongly depend on the precursors. The goal of this work was to follow, using nuclear magnetic resonance (NMR), the evolution of the local environments of both silicon and aluminum atoms, during the whole elaboration process of cordierite. Three preparations were chosen as representative of different crystallization behaviors: the hydrolysis–condensation processes were studied by ^{29}Si and ^{27}Al liquid NMR. The structure of the dried gels was characterized by ^{29}Si and ^{27}Al magic angle spinning (MAS) NMR. Then the thermal behavior up to 1000 °C was followed by X-ray diffraction

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Table I. Various Sol–Gel Preparations for Cordierite

preparations	Si precursor	Al precursor	Mg precursor	ref
one alkoxide	$Si(OEt)_4$	$Al(NO_3)_3 \cdot 9H_2O$	$Mg(NO_3)_2 \cdot 6H_2O$	3, 4, 6, 7
	ethyl silicate	$Al_2(OH)_5Cl \cdot H_2O \cdot CH_3CH(OH)CH_2OH$	$MgCl_2 \cdot 6H_2O$	5
	$Si(OEt)_4$	$AlCl_3 \cdot 6H_2O$, $Al(OH)(OOCH)(OOCCH_3)$	$MgCl_2 \cdot 6H_2O$, $Mg(CH_3COO)_2$, $MgSO_4$	6
two alkoxides	$Si(OEt)_4$	$Al(OBu^s)_3$	$Mg(CH_3COO)_2 \cdot 4H_2O$	8, 10
	$Si(OEt)_4$	$Al(OBu^s)_3$	$Mg(NO_3)_2 \cdot 6H_2O$	9, 11
	$Si(OEt)_4$	$Al(OBu^s)_3$	$MgCl_2 \cdot 6H_2O$	12
three alkoxides	$Si(OEt)_4$	$Al(OPr^i)_3$	$Mg(OEt)_2$	14, 15
	$Si(OEt)_4$	$Al(OBu^s)_3$	$Mg(OEt)_2$	7, 19
	$Si(OEt)_4$	$Mg[Al(OEt)_4]_2$		16, 17
	$Si(OEt)_4$	$Al(OBu^s)_3$	Mg flakes	20, 21

Table II. Sol–Gel Preparations for Cordierite Used in the Present Study

preparations		Si precursor	Al precursor	Mg precursor	solvt	gelation time	gel aspect
one alkoxide	NNE	$Si(OEt)_4$	$Al(NO_3)_3 \cdot 9H_2O$	$Mg(NO_3)_2 \cdot 6H_2O$	ethanol	≈3 months	transparent
two alkoxides	NAP	$Si(OEt)_4$	$Al(OBu^s)_3$	$Mg(NO_3)_2 \cdot 6H_2O$	2-propanol	immediate	white gels; precipitates
	AAP	$Si(OEt)_4$	$Al(OBu^s)_3$	$Mg(OAc)_2 \cdot 4H_2O$	2-propanol	immediate	white gels; precipitates
	NCE	$Si(OEt)_4$	$Al(OBu^s)_2(etac)$	$Mg(NO_3)_2 \cdot 6H_2O$	ethanol	1–2 h	translucent
	NCP	$Si(OEt)_4$	$Al(OBu^s)_2(etac)$	$Mg(NO_3)_2 \cdot 6H_2O$	2-propanol	≈2 h	translucent
	ACE	$Si(OEt)_4$	$Al(OBu^s)_2(etac)$	$Mg(OAc)_2 \cdot 4H_2O$	ethanol	≈3 h[a]	transparent
	ACP	$Si(OEt)_4$	$Al(OBu^s)_2(etac)$	$Mg(OAc)_2 \cdot 4H_2O$	2-propanol	≈6 h	
Si–Al ester	NEE	$Si(OEt)_4$	$(EtO)_3SiOAl(OBu^s)_2$	$Mg(NO_3)_2 \cdot 6H_2O$	ethanol	immediate	white gels; precipitates
	NEP	$Si(OEt)_4$	$(EtO)_3SiOAl(OBu^s)_2$	$Mg(NO_3)_2 \cdot 6H_2O$	2-propanol	immediate	white gels; precipitates
	AEE	$Si(OEt)_4$	$(EtO)_3SiOAl(OBu^s)_2$	$Mg(OAc)_2 \cdot 4H_2O$	ethanol	immediate	white gels; precipitates
	AEP	$Si(OEt)_4$	$(DEtO)_3SiOAl(OBu^s)_2$	$Mg(OAc)_2 \cdot 4H_2O$	2-propanol	≈50 h[a]	transparent

[a] For these preparations, a first gelation occurs when the aqueous solution is added to the alkoxide solution, but with stirring, a clear sol can be obtained that will gel afterward.

(XRD) as well as MAS NMR. This study shows that the structure of the gel greatly influences the thermal behavior of the system and the crystallization temperature of the cordierite phase.

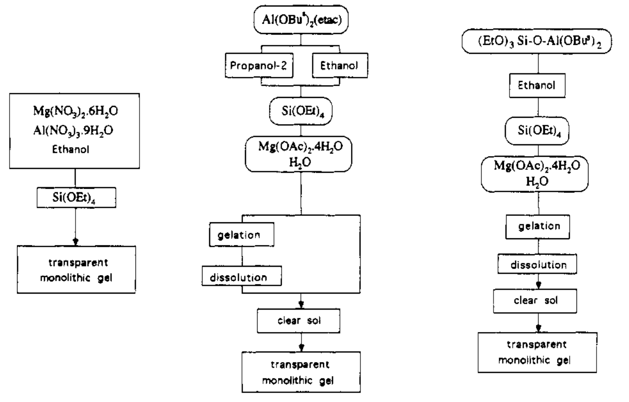
II. Experimental Section

Gel Preparations. Various sol–gel preparations for cordierite have been tested. They can be divided into three categories: preparation with one alkoxide, preparation with two alkoxides, and preparation with a mixed silicon–aluminum ester. Silicon tetraethoxide, TEOS [$Si(OEt)_4$] (Dynamit Nobel), was used for all the preparations. For the Al precursors, aluminum *sec*-butoxide [$Al(OBu^s)_3$] (Alfa), aluminum *sec*-butoxide modified with ethyl acetoacetate [$Al(OBu^s)_2(etac)$] (Alfa) and nitrate [$Al(NO_3)_3 \cdot 9H_2O$] (Prolabo) were used. A mixed Si–Al ester was also used, $(OEt)_3Si{-}O{-}Al(OBu^s)_2$ (Dynamit Nobel). Mg precursors were acetate [$Mg(OAc)_2 \cdot 4H_2O$)] and nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] (Prolabo). The preparations are labeled with three letters, the first one refers to the Mg precursor (N for nitrate or A for acetate), the second refers to the Al precursor (N for nitrate, A for alkoxide, C for alkoxide chelated with etac or E for the Si–Al ester), and the last letter refers to the solvent (E for ethanol or P for 2-propanol) (Table II).

The goal of this work was to correlate (using liquid NMR) the reactions that occur during the hydrolysis process with the evolution of the gels during heat treatment. Thus, synthesis leading to precipitates or translucent sols were not considered any further. Three preparations were selected for detailed investigation: the preparation with one alkoxide (NNE), one with two alkoxides either in ethanol (ACE) or 2-propanol (ACP) and one with the Si–Al ester (AEE).

Schematic diagrams of these preparations are presented in Figure 1. The various proportions of precursors, water, and solvent are listed in Table III. For the NNE preparation (Figure 1a), a solution of magnesium (1.37 g) and aluminum (4.00 g) nitrates in ethanol (6.56 g) was prepared. Then TEOS (2.78 g) was added with stirring. No additional water was used since the amount of water introduced with the nitrates (48 H_2O/equiv of $Mg_2Al_4Si_5O_{18}$ or 9.6 H_2O/Si) is enough to hydrolyze all the ethoxy groups of TEOS. Gelation takes place after about 3 months in a closed vessel.

For the ACE and ACP preparations (Figure 1b), TEOS (4.31 g) was added to an alcoholic solution (ethanol or 2-propanol, 9.95 g) of the aluminum-modified alkoxide, $Al(OBu^s)(etac)$ (5 g). An aqueous solution of magnesium acetate was prepared (1.77 g of acetate for 1.79 g of H_2O) so that the number of water molecules introduced into the alkoxide mixture corresponds to the amount of alkoxy groups to hydrolyze, i.e., 32 H_2O/equiv of $Mg_2Al_4Si_5O_{18}$. Various equivalent $Mg_2Al_4Si_5O_{18}$ concentrations were tried by adjusting the alcohol amount. In 2-propanol, for concentrations ranging from 6 to 10 wt %, clear monolithic gels were obtained within 4–7 h. For higher concentrations up to 12 wt %, a first gelation took place immediately after the addition of the acetate solution. Upon stirring, this gel dissolves back to a clear solution that leads to transparent monolithic gels within ≈3 h. Increasing the concentration to 12.5 wt % gave white gels immediately. When ethanol was used instead of 2-propanol, whatever the concentration was, from 7.6 to 12.8 wt %, no immediate gelation took place and monolithic transparent gels were obtained. For a 10.6 wt % concentration, the gelation time was ≈6 h.



a - NNE b - ACP or ACE c - AEE

Figure 1. Schematic diagrams of the preparation of cordierite gels: (a) NNE, (b) ACE and ACP, and (c) AEE.

For the AEE preparation (Figure 1c), 10 g of the mixed Si–Al ester, $(OEt)_3Si{-}O{-}Al(OBu^s)$ in ethanol (21.55 g), is mixed with TEOS (1.48 g) to reach a Si/Al stoichiometry of 5/4. This mixture is then hydrolyzed with an aqueous solution of magnesium acetate (3.04 g of acetate for 3.067 g of H_2O), as described in the previous preparation. For a 10.6 wt % concentration and 32 mol of H_2O/equiv of $Mg_2Al_4Si_5O_{18}$, a first gelation took place immediately. The gel redissolved in less than 20 h to give a clear sol. Gelation

Table III. Compositions of the Various Sol-Gel Preparations for Cordierite

preparations	precursors (molar ratios)				$H_2O/Mg_2Al_4Si_5O_{18}$ ratio	equivalent $Mg_2Al_4Si_5O_{18}$ concentration (wt %)
NNE	$Mg(NO_3)_2{\cdot}6H_2O$ (2)	$Al(NO_3)_3{\cdot}9H_2O$ (4)	TEOS (5)	ethanol (53.3)	48	10.6
ACE	$Mg(OAc)_2{\cdot}4H_2O$ (2)	$Al(OBu^s)_2(etac)$ (4)	TEOS (5)	ethanol (52.3)	32	10.6
ACP	$Mg(OAc)_2{\cdot}4H_2O$ (2)	$Al(OBu^s)_2(etac)$ (4)	TEOS (5)	2-propanol (40.0)	32	10.6
AEE	$Mg(OAc)_2{\cdot}4H_2O$ (2)	$(EtO)_3SiOAl(OBu^s)_2$ (4)	TEOS (1)	ethanol (66.0)	32	10.6

with the formation of a transparent monolithic gel took place after ≈50 h.

Characterization Techniques. NMR spectra were recorded using a Bruker MSL400 spectrometer. Liquid experiments were run in 10-mm tubes with an inner tube containing the deuterated solvent ($CDCl_3$). Typical pulsewidths were 5 μs for ^{29}Si and 10 μs for ^{27}Al with delays between pulses of 6 s for ^{29}Si and 0.5 s for ^{27}Al. 300 and 50 scans were recorded respectively for ^{27}Al and ^{29}Si NMR spectra. For the MAS experiments, powders were packed into zirconia rotors and spun at ≈4 kHz. 2- and 2.5-μs pulses were respectively applied for the ^{27}Al and ^{29}Si MAS NMR experiments with delays between pulses of 2 and 60 s. 1000–1500 scans were recorded for ^{27}Al NMR spectra and 500–1000 scans for ^{29}Si NMR spectra. The usual notation will be used for Si sites, Qx,y where x refers to the number of bridging O atoms and y to the number of AlO_4 tetrahedra surrounding the Si atom.

DTA and TGA were performed using a Netzsch STA 409 equipment. The heating rate was 5 °C/min. The xerogels were heat treated under air flow in a tubular furnace with heating rates of 250 °C/h up to a temperature 50 °C below the maximum temperature, T_m, and then 100 °C/h up to T_m where the temperature was maintained. XRD patterns were recorded on a Philips XRD model using the Cu Kα radiation.

III. Results and Discussion

Liquid ^{27}Al and ^{29}Si NMR Studies. The hydrolysis processes for the three preparations NNE, ACE and AEE were followed by ^{27}Al and ^{29}Si liquid-state NMR to study possible reactions occurring between the precursors. The concentration of the various solutions is 10.6 wt % of equivalent $Mg_2Al_4Si_5O_{18}$.

Hydrolysis Process of the Preparation NNE. The ^{27}Al NMR spectrum recorded 6 min after the addition of the ethanolic solution of hydrated nitrates into the ethanolic solution of TEOS shows one sharp peak at 0.6 ppm (Figure 2a). It is similar to the spectrum of a solution of aluminum nitrate and is characteristic of aquo species, $[Al(H_2O)_{6-n}(OH)_n]^{3+}$. No evolution is noticed after 110 min. The ^{29}Si NMR spectrum of the hydrolyzed solution recorded only 20 min after addition of water no longer shows the signal for TEOS at −82.2 ppm. Broad components at −91.5 and −100 ppm (Figure 2b) can be hardly distinguished, overlapped by a broad signal centered at −110 ppm due to the glass tube and the probe. Those values reported for the hydrolysis process of pure TEOS[22] correspond to Q_2 and Q_3 condensed species. Therefore it seems that TEOS hydrolyzes and condenses quite rapidly under the preparation conditions. This phenomenon can be assigned to a catalytic effect of the solution of nitrates. For the present preparation, the ethanolic solution of nitrates exhibits a "pH" of ≈0.9, revealing a partial hydrolysis of the cations. Due to the higher acidity of Al^{3+} ions compared to Mg^{2+} ions, Al salts are certainly hydrolyzed preferentially.[23]

Thus, no reaction seems to occur between the Al and Si precursors under the present experimental conditions.

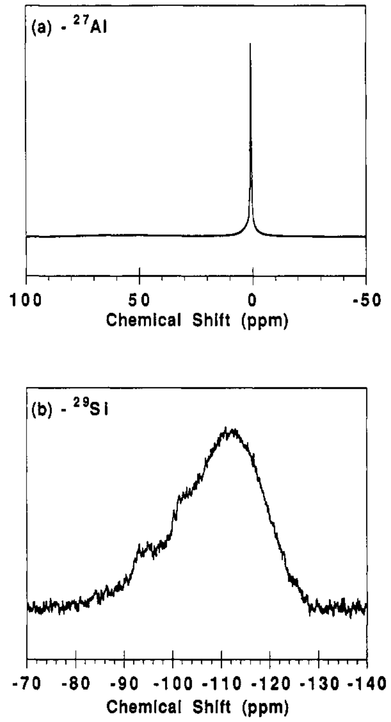


Figure 2. Liquid NMR spectra of the NNE preparation after hydrolysis. (a) ^{27}Al NMR spectrum at t = 6 min and (b) ^{29}Si NMR spectrum at t = 20 min.

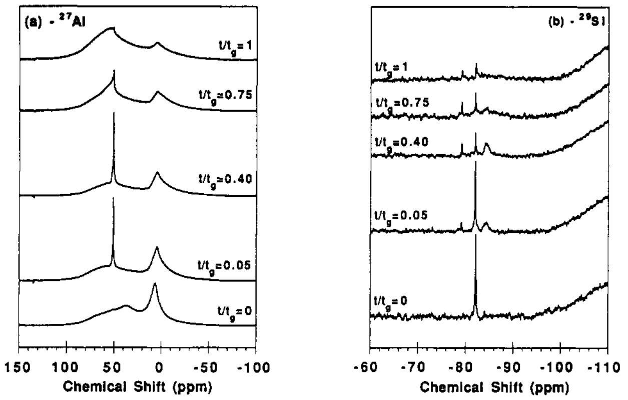


Figure 3. Evolution of (a) ^{27}Al and (b) ^{29}Si NMR spectra of the ACE preparation during the hydrolysis process.

Hydrolysis Process of the Preparation ACE. The experiments were done using the ACE preparation and not the ACP, because the latter system gives rise to a first gelation phenomenon.

The ^{27}Al spectrum of the solution $Al(OBu^s)_2(etac)/TEOS/EtOH$ before hydrolysis shows two broad signals at 6.4 and 35.7 ppm (Figure 3a). The structure of the pure alkoxide has already been discussed in a previous paper.[24] It presents a signal due to hexacoordinated Al atoms at ≈0 ppm and one assigned to tetracoordinated atoms at ≈50–60 ppm.[24] The predominance of hexacoordinated

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sites is due to the chelating nature of the etac ligand. When diluted in *sec*-butyl alcohol the component due to tetracoordinated Al atoms increases and this reveals that an equilibrium exists between several species. Dilution shifts the equilibrium towards the formation of smaller species in which the 4-fold coordination is favored. When the modified aluminum alkoxide is diluted in ethanol, a strong increase of a component around 35 ppm can be seen: this value is usually assigned to pentacoordinated atoms.[25,26] The change in the NMR spectrum of the alkoxide in ethanol is due to exchange reactions between butoxy and ethoxy groups as evidenced by ^{13}C NMR, leading to the formation of mixed species, $Al(OBu^s)_{2-x}(OEt)_x$. The presence of Al–OEt bonds seems to favor the formation of pentacoordinated Al atoms as evidenced by the observation of a 36 ppm chemical shift for $Al(OEt)_3$.[27] A complete study of the alcoholysis and hydrolysis reactions of this modified alkoxide will be published. The ^{29}Si NMR spectrum of the ACE solution exhibits the signal of pure TEOS at −82.2 ppm (Figure 3b).

The evolution of the NMR spectra of the ACE preparation after hydrolysis with an aqueous solution of magnesium acetate is represented in Figure 3. The time is indicated by reference to the gelation time t_g, which is ≈6 h. Almost immediately after hydrolysis ($t/t_g = 0.05$), the ^{27}Al NMR spectrum is completely modified: the signal due to hexacoordinated atoms is still present, but together with two components in the tetracoordinated Al range: a broad signal around 55 ppm and a very sharp peak at 50.5 ppm. The signal assigned to pentacoordinated atoms at ≈35 ppm has disappeared. When the hydrolysis–condensation reactions proceed, a second sharp peak appears at 51.8 ppm. Both sharp peaks progressively disappear and at the gelation point, two broad signals are present at ≈4 and ≈51 ppm. The two sharp peaks are related to the presence of tetrahedral Al atoms in a highly symmetric environment. A similar peak has already been reported[28] for the hydrolysis of the ester $(OEt)_3Si{-}O{-}Al(OBu^s)_2$. The chemical shift value could suggest the presence of Al–O–Si bonds.[29] Possible species could be $Al\{O[Si(OR)_3]\}_4$ with R = H, Et, or Bu^s. They could form a nucleus for the growth of a silicoaluminate network. These species are transient and never represent more than 10% of the total Al sites. The main point shown by the ^{27}Al NMR spectra, is the increase, during the condensation process, of the amount of tetracoordinated Al atoms with chemical shift value around 55 ppm typical of that found for cordierite.[30]

At $t/t_g = 0.5$, the ^{29}Si NMR spectrum shows two new signals at −79.2 and −84.3 ppm assigned respectively to the hydrolyzed species, $Si(OEt)_3OH$, and to the condensed species $Si(OAl)(OR)_3$.[31] Various combinations of R (H, Et, or Bu^s) could be present and account for the broadness of the peak. During the hydrolysis–condensation process, the peak due to TEOS decreases even if a small amount is still present at the gelation point. The amount of hydrolyzed species first increases and then decreases. The signal due to condensed species also increase, broaden and the signal is lost under the baseline. The most interesting point is that only the monohydrolyzed species are detected at the same time as condensed species containing Si–O–Al bonds are formed. A possible explanation is that as soon as TEOS is hydrolyzed, it reacts with hydrolyzed Al species to form an Al–O–Si bond according to

$$Al{-}OH + HO{-}Si(OEt)_3 \rightarrow Al{-}O{-}Si(OEt)_3 + H_2O$$

Direct reaction of TEOS with Al–OH and removal of ethanol is also possible. These reactions could explain the formation of species such as $Al\{O[Si(OR)_3]\}_4$ that can afterward undergo hydrolysis and condensation to build a silicoaluminate network.

Thermal Behavior of Selected Xerogels and XRD Analysis of Heat-Treated Samples. The TG and DTA curves of the NNE and ACP gels are presented in Figure 4 and the variation with heat treatment of the XRD patterns in Figure 5. The results for the ACE and AEE gels are similar to those obtained for ACP gels.

The NNE xerogel shows a continuous weight loss of 54.8% from 75 to 500 °C (Figure 4a). The DTA curve presents several endothermic peaks below 500 °C, a sharp one at 75 °C, a broad one centered around 150 °C, and a shoulder around 450 °C (Figure 4b). Two weak exothermic phenomena are present at 800 and 1010 °C. The XRD pattern of the NNE xerogel shows peaks due to crystalline aluminum and magnesium nitrates, $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (Figure 5a). After heat treatment at 800 °C, broad peaks due to poorly crystalline $MgAl_2O_4$ spinel are present. At 1000 °C, the main crystalline phase is μ-cordierite, but the spinel is still present.

The thermal phenomena detected in the DTA curve can be assigned as follows: the sharp endothermic peak at 75 °C can be due to dehydration of the crystallized nitrates (XRD analysis on a xerogel freshly dried at 100 °C gives an amorphous pattern). The endotherms that follow at 150 and 450 °C, and that correspond to weight losses in the TG curve, could be assigned respectively to loss of solvent trapped in the xerogel and decomposition of nitrates. The weak exothermic peak at 800 °C is certainly due to the crystallization of the spinel phase, $MgAl_2O_4$ while the exothermic peak at 1010 °C should be related to the crystallization of the metastable μ-cordierite phase.

The thermal behavior of the ACP xerogel, as well as those of ACE and AEE xerogels, are completely different from the behavior of the NNE xerogel. The TG curve shows a total weight loss of 51.5% with two main stages, from room temperature to ≈300 °C (36%) and from ≈300 to ≈550 °C (14%) (Figure 4c). These two weight losses are respectively associated to an endothermic peak and an exothermic peak in the DTA curve (Figure 4d). At higher temperatures, the DTA curve shows an endothermic peak at ≈860 °C, followed by two exothermic peaks at 970 and 1005 °C. The XRD analysis for ACP, ACE, or AEE xerogels always shows the same crystallization sequence (Figure 5b). The xerogel is amorphous. The first crystalline phase, the μ-cordierite, appears after heat treatment of the xerogel at 900 °C for 1 h. After 5 h at 1000 °C, the XRD pattern shows only peaks due to the α-cordierite phase. The thermal phenomena revealed by the DTA curve most likely correspond to loss of solvent for the first

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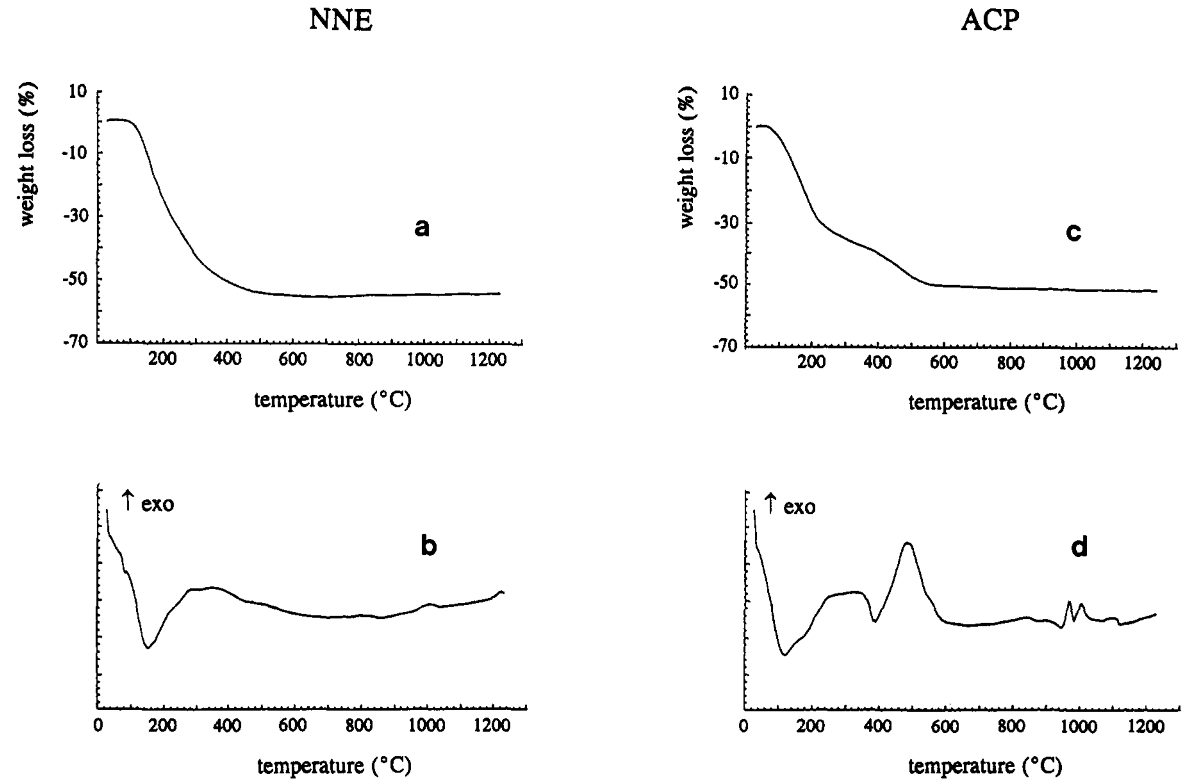

Figure 4. TG and DTA curves of NNE gel (a and b) and ACP gel (c and d).

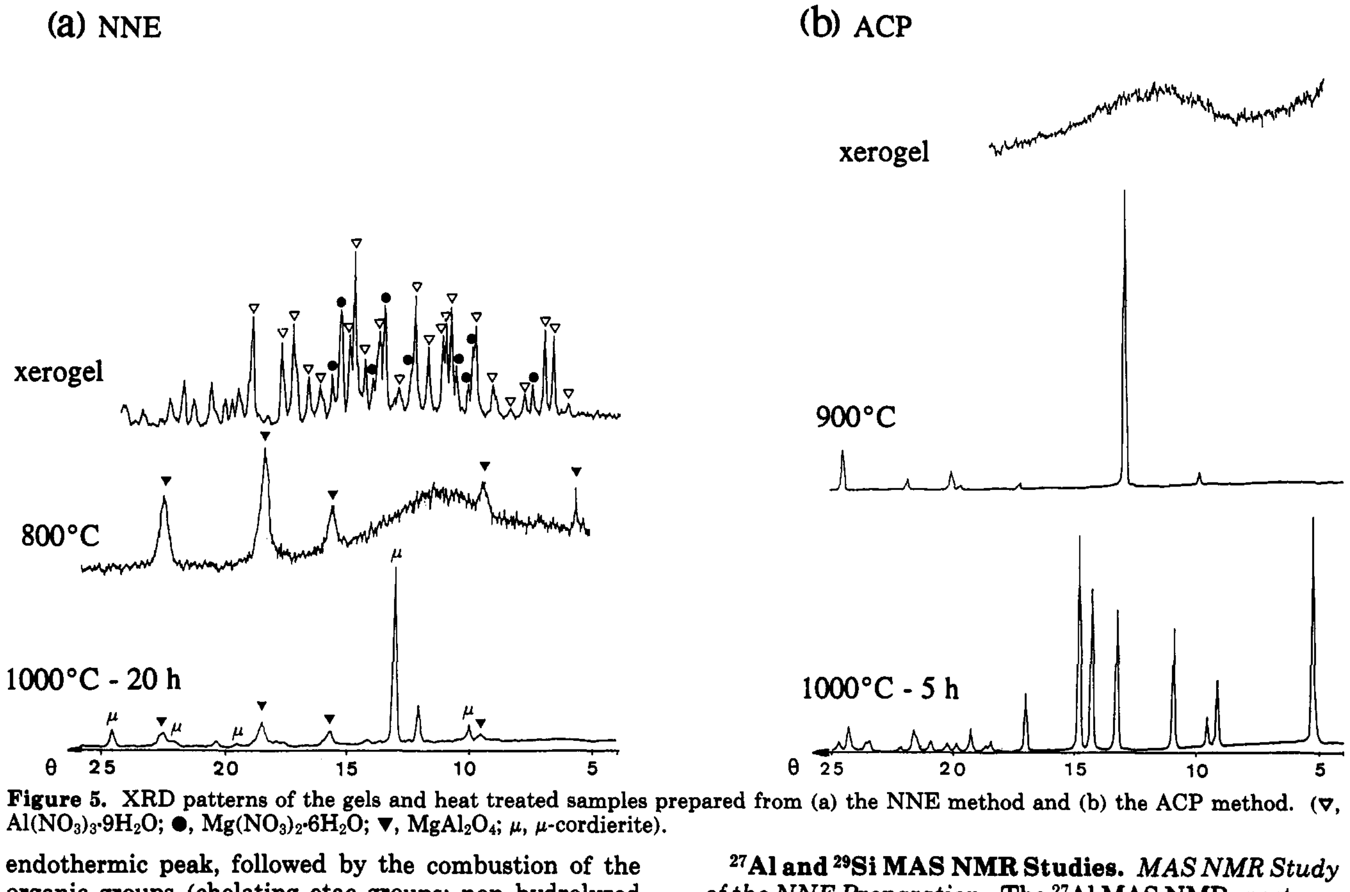

Figure 5. XRD patterns of the gels and heat treated samples prepared from (a) the NNE method and (b) the ACP method. (▽, $Al(NO_3)_3{\cdot}9H_2O$; ●, $Mg(NO_3)_2{\cdot}6H_2O$; ▼, $MgAl_2O_4$; μ, μ-cordierite).

endothermic peak, followed by the combustion of the organic groups (chelating etac groups; non hydrolyzed alkoxy groups). At 970 and 1005 °C, the two exothermic peaks correspond to the crystallization of μ-cordierite and the transformation from μ- to α-cordierite. The crystallization peaks were respectively found at 980 (μ) and 1030 °C (α) for the ACE xerogel and at 980 (μ) and 1010 °C (α) for the AEE xerogel.

^{27}Al and ^{29}Si MAS NMR Studies. *MAS NMR Study of the NNE Preparation.* The ^{27}Al MAS NMR spectrum of the NNE xerogel (Figure 6a) presents a main component at −3.4 ppm due to aluminum atoms in an octahedral symmetry. It corresponds to the chemical shift of aluminum nitrate whose presence was detected by XRD analysis. The ^{29}Si MAS NMR spectrum of the same xerogel (Figure 6b) presents two peaks at −102.8 and −109.7

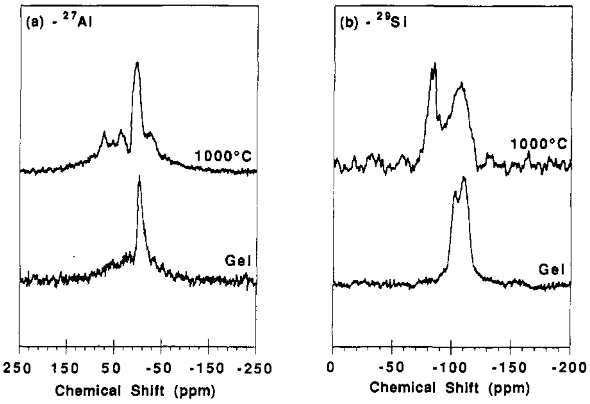

Figure 6. (a) ^{27}Al and (b) ^{29}Si MAS NMR spectra of the NNE gel and gel heated at 1000 °C.

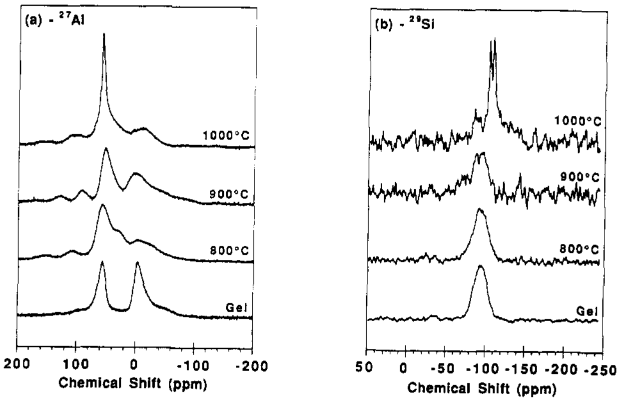

Figure 7. (a) ^{27}Al and (b) ^{29}Si MAS NMR spectra of the ACE gel and gel heated at various temperatures.

ppm. This spectrum is similar to that of a silica gel obtained from hydrolysis of TEOS. The two peaks are due to $Q_{3,0}$ and $Q_{4,0}$ silicon sites.[32,33] These NMR spectra do not show evidence for reaction between precursors. The NNE xerogel can be described as an amorphous silica matrix with aluminum and magnesium nitrates.

When heated at 1000 °C, the NNE sample exhibits a more complex ^{27}Al MAS NMR (Figure 6a). The main peak is still due to aluminum in octahedral sites with a chemical shift at 6 ppm. Other components appear at 30 and 70 ppm that can be assigned to pentacoordinated and tetracoordinated Al sites as already mentioned for similar cordierite preparation. However, in the present spectrum, overlaps with spinning side bands and probe signal give uncertainty as to the present assignment. The presence of octahedral sites agrees with the XRD results that show $MgAl_2O_4$ spinel at this temperature. The reported chemical shift value for this phase is 0 ppm.[30] The ^{29}Si MAS NMR spectrum of the same sample (Figure 6b) shows a broad signal centered on −107.6 ppm and two sharper peaks at −81.7 and −84.3 ppm. The broad signal corresponds to an amorphous silica network.[32] The shift of the two other peaks downfield may be due to the presence of Si–O–Al bonds for these Si sites.[34–36] The chemical shift values are in agreement with SiO_4 tetrahedra bonded to 3 or 4 AlO_4 tetrahedra.

MAS NMR Studies of the ACE and AEE Preparations. The ^{27}Al and ^{29}Si MAS NMR spectra have been recorded on the ACE and AEE xerogels as well as heat treated samples at 800, 900, and 1000 °C. The evolution of the spectra are quite similar for the two series; thus only the spectra for the ACE preparation are presented (Figure 7).

The ^{27}Al MAS NMR spectrum of the ACE xerogel shows two peaks at 55.9 and −0.3 ppm respectively due to tetrahedral and octahedral Al sites (Figure 7a). The octahedral sites can be related to the presence of chelating ethylacetoacetate (etac) groups still bonded to Al atoms as revealed by IR (ν(C–C–C) at 1535 cm^{-1}) and by ^{13}C CP MAS NMR spectrum (peaks at 24.3 ppm (CH_3–C–O–Al), at 73.6 ppm (Al–O–$CH(CH_3)C_2H_5$), at 174.4 ppm (Al–O–*C*(OEt)CH–) and at 187 ppm (Al–O–*C*(CH_3)CH–)). The presence of bidentate ligands bonded to Al obviously increases the coordination number of Al. The most interesting point is the rather intense peak at 55.1 ppm, a chemical shift value close to what is found for crystalline α-cordierite, in which all AlO_4 tetrahedra are surrounded by four SiO_4 tetrahedra.[30,37] The ^{29}Si MAS NMR spectrum (Figure 7b) shows a broad peak centered at ≈−92 ppm. This value is shifted downfield compared to the value for a silica gel or what was found in the NNE xerogel. Such a shift occurs when the number of AlO_4 tetrahedra around the SiO_4 tetrahedron increases. Many data have been reported in literature on the ^{29}Si MAS NMR of aluminosilicates.[34–36] A distribution of Si sites leads to a broadening of the peak and thus it is quite difficult to tell how many Al–O–Si bonds exist around each Si. A chemical shift value of ≈−92 ppm should correspond to an average value of 2–3 Al–O–Si bonds assuming a fully condensed network. The spectrum recorded with cross-polarization does not exhibit any change compared to the single-pulse experiment, showing a uniform distribution of the protons within the samples.

According to these NMR results, reactions seem to have occurred between the silicon alkoxide and the modified aluminum alkoxide to form Si–O–Al bonds. To get clear evidence of such reactions, ^{27}Al MAS NMR spectra (Figure 8) were recorded on three different gels prepared from hydrolysis of (i) $Al(OBu^s)_2(etac)$ only, (ii) $Al(OBu^s)_2(etac)$, and $Mg(OAc)_2{\cdot}4H_2O$, and (iii) $Al(OBu^s)_2(etac)$, $Mg(OAc)_2{\cdot}4H_2O$ and TEOS. The chemical compositions of the starting solutions were $Al(OBu^s)_2(etac)/H_2O/EtOH$ 1/8/20.3, $Al(OBu^s)_2(etac)/Mg(OAc)_2{\cdot}4H_2O/H_2O/EtOH$ 1/0.5/8/18.7, and $Al(OBu^s)_2(etac)/Mg(OAc)_2{\cdot}4H_2O/TEOS/H_2O/EtOH$ 1/0.5/1.25/8/26.1. The spectrum of the alumina gel (Figure 8a) exhibits a main peak at 3.5 ppm typical of octahedral aluminum sites in agreement with previous studies.[38] The spectrum of the gel prepared from modified aluminum *sec*-butoxide and magnesium acetate is quite similar with a main peak centered at 3.9 ppm, even if a slight downfield dissymetry could reveal the presence of some tetrahedral sites. The spectrum obtained for the cordierite preparation (Figure 8c) is totally different with two components: one peak at −0.2 ppm due to octahedral sites, but also an intense peak at 56.2 ppm, due to tetrahedral sites. The comparison of these three gels shows clearly that the reaction of the modified aluminum alkoxide

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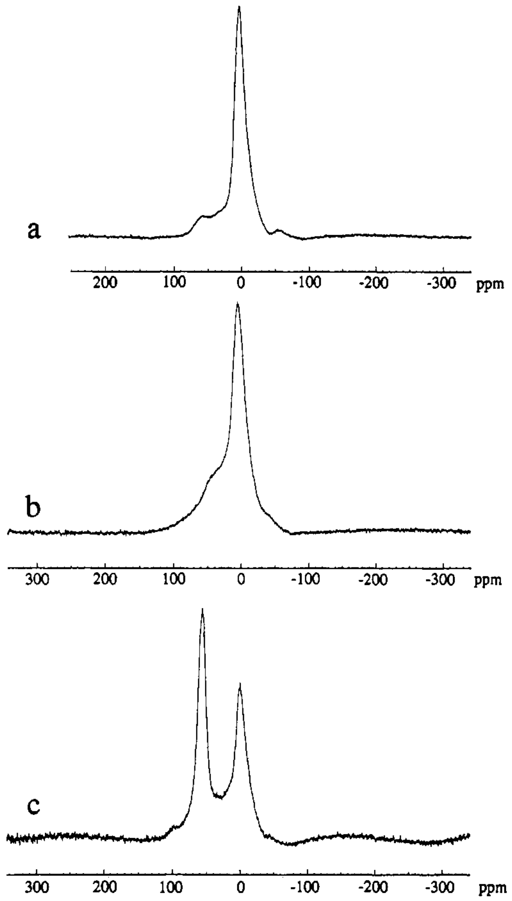

Figure 8. ^{27}Al MAS NMR spectra of gels prepared from (a) $Al(OBu^s)_2(etac)$, (b) $Al(OBu^s)_2(etac)$, and $Mg(OAc)_2{\cdot}4H_2O$, and (c) $Al(OBu^s)_2(etac)$, $Mg(OAc)_2{\cdot}4H_2O$ and TEOS.

with TEOS gives rise to the formation of tetracoordinated aluminum sites. Resonance peaks for tetrahedral sites in alumina network are usually found around 65–70 ppm.[38] The highfield shift observed in the present sample is certainly due to the presence of Si–O–Al bonds.

A gel of the cordierite composition prepared according to the ACE, ACP or AEE methods can thus be considered as an amorphous aluminosilicate network.

The MAS NMR spectra of the ACE heated gels have been studied (Figure 7). The sample heated at 800 °C for 1 h is amorphous while the two other samples heated at 900 °C for 1 h and at 1000 °C for 5 h show crystalline phases, respectively, μ-cordierite and α-cordierite (with some traces of μ).

The ^{27}Al MAS NMR spectra of the samples heated at 800 and at 900 °C are quite complex since spinning sidebands and probe signal overlap the sample signals (Figure 7a). However, they show a decrease of the peak due to hexacoordinated Al atoms and an increase of the peak due to tetracoordinated Al sites. After a heat treatment at 1000 °C for 5 h, the sample seems to contain only tetracoordinated Al atoms. A spectrum was recorded at 130 MHz, with a signal-free probe, and a 11-kHz spinning rate (Figure 9). It does not show any evidence of hexacoordinated Al atoms and confirms the absence of hexacoordinated Al atoms in a fairly symmetric sites. However, strongly distorded Al sites could be present, leading to too broad signals to be detected. This spectrum suggests the presence of two kinds of tetracoordinated atoms with a sharp peak at 56.6 ppm and a broader component around 40 ppm. These values are in agreement with those reported for cordierite phases.[30,37]

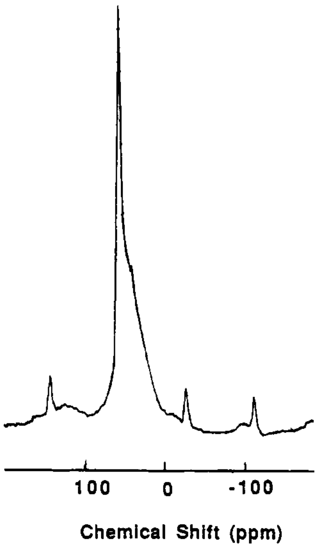

Figure 9. ^{27}Al MAS NMR spectra of the ACE gel heated at 1000 °C for 5 h (frequency 130 MHz; spinning rate 11 kHz).

The ^{29}Si MAS NMR spectrum of the sample heated at 800 °C is quite similar to the spectrum of the xerogel with a broad signal centered on −93 ppm (Figure 7b). The local environment of Si sites does not seem to change up to 800 °C in the amorphous phase. The NMR spectrum of the sample heated at 900 °C for 1 h, corresponding to μ-cordierite, exhibits a very bad signal/noise ratio, even when the delay between pulses is increased up to 100 s. The NMR spectrum of the sample heated to 1000 °C for 5 h and corresponding to α-cordierite is totally different. It can be divided in two groups of signals: a group of four peaks, two intense at −101.3 and −106.2 ppm and two smaller at −96.3 and −114.3 ppm and a group of three small peaks at −80.2, −82.6, and −86.0 ppm. This spectrum is similar to the one already published for α-cordierite.[37] The two groups correspond respectively to Si sites Qx,y located in either rings ($1 \leq x \leq 4$) or chains ($2 \leq x \leq 4$) of the cordierite structure. The various components in each group correspond to the various combinations of AlO_4 and SiO_4 tetrahedra surrounding one SiO_4 tetrahedron.

IV. Summary

Three sol–gel preparations for cordierite were studied: the chemical reactions occurring during the hydrolysis–condensation process in the liquid state and during the heat treatment of gels, characterized by ^{27}Al and ^{29}Si NMR.

A gel was prepared from silicon ethoxide, aluminum, and magnesium nitrates (NNE). No reaction between the various precursors seems to have occurred during the hydrolysis–condensation process. The aluminum species present in solution is the aquo species $[Al(H_2O)_6]^{3+}$, very stable in acidic medium. Deprotonation cannot occur spontaneously at room temperature to lead to the formation of Al–OH groups, which could further condense. Thus no Si–O–Al bonds can be formed under these experimental conditions. The only role played by the solution of nitrates is to catalyse the condensation of TEOS. The gel appears as a silica network with aluminum and magnesium ions dispersed in it. In this case, aluminum atoms are in octahedral environment, such as in $MgAl_2O_4$ spinel. During the heat treatment, aluminum and magnesium atoms react to form this phase, and at 800 °C, the system presents a phase separation between crystalline spinel and amorphous silica. Then, these two phase react together to form μ-cordierite. At 1000 °C, the spinel is still present and the α-cordierite is not yet formed.

The other preparations are based on silicon ethoxide, a modified aluminum alkoxide or a mixed silicon–aluminum alkoxide, and magnesium acetate (ACE, ACP and AEE). Their behaviors are quite similar. In these cases, ^{27}Al and ^{29}Si liquid and MAS NMR experiments show the formation of Si–O–Al bonds during the hydrolysis–condensation reactions. The condensation occurs via Al–OH groups which are easily formed due to the high reactivity of aluminum alkoxides towards hydrolysis. The reaction that seems likely to occur is the following:

$$\text{Al–OH} + \text{RO–Si(OR)}_3 \rightarrow \text{Al–O–Si(OR)}_3 \quad (\text{R} = \text{H, Et, Bu}^s)$$

The formation of such bonds is closely related to the change in aluminum coordination, which switches from 6 to 4. Al atoms are usually hexacoordinated in alumina gels, but in the present case, they appear mainly tetracoordinated in the gel, as in the crystalline α-cordierite phase. Gels can thus be described as silicoaluminate networks. During the heat treatment, the spinel phase does not form. The presence of a glasslike transition around 860 °C shows that the system can be considered as a cordierite glass at this temperature. Then at 900 °C, the μ-cordierite is the first phase to crystallize, and then transforms at 1000 °C into pure α-cordierite.

The different thermal behaviors of these cordierite preparations come from the different gel structures. This study shows the importance of the formation of Si–O–Al bonds in solution during the hydrolysis–condensation process, that is closely related to a change in the coordination state of aluminum sites.

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