A SYNTHETIC Na-RICH MICA: SYNTHESIS AND CHARACTERIZATION BY [27]Al AND [29]Si MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Abstract—A swelling mica, $Na_2Mg_3(Al_2Si_2)O_{10}F_2 \cdot xH_2O$, (hereafter "Na-4 mica") was synthesized from metakaolinite + MgO and Mg aluminosilicate gels at different temperatures and durations using NaF flux. The various samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and [27]Al and [29]Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The results showed that phase-pure Na-4 mica was obtained from metakaolinite which serves as a cost-effective aluminosilicate source. ^{27}Al MAS NMR spectra showed that all or nearly all Al is in tetrahedral coordination whereas ^{29}Si MAS NMR spectra showed that the nearest neighbor environment of Si is mainly Si(3Al), as expected based on the Si:Al ratio.

Key Words—KGa-1, MAS NMR Spectroscopy, Metakaolinite, Mica, Na Mica, Synthetic Clay Mineral.

INTRODUCTION

The synthetic clay mineral, "Na-4-mica" (Gregorkiewitz *et al.*, 1974; Gregorkiewitz and Rausell-Colom, 1987; Herrero *et al.*, 1987), contains four Na^+ ions per unit cell and has a theoretical cation exchange capacity of 468 meq/100 g on an anhydrous basis. This synthetic clay mineral, ideally $Na_4Si_4Al_4Mg_6O_{20}F_4 \cdot xH_2O$, has a high [IV]Al content but exhibits unusual swelling behavior and selective cation exchange properties (Gregorkiewitz and Rausell-Colom, 1987; Paulus, 1990; Paulus *et al.*, 1992; Komarneni *et al.*, 1991, 1998; Franklin and Lee, 1996) potentially useful in hazardous cation separations for waste disposal or metal recovery from dissolved ores. The unusual swelling behavior was attributed (Gregorkiewitz and Rausell-Colom, 1987) to the high number of interlayer Na^+ ions per unit cell, which are accommodated in the ditrigonal holes by an offset layer stacking of $b/3$.

The structural features and initial cation exchange properties were studied by using millimeter-sized flakes (Gregorkiewitz and Rausell-Colom, 1987). These flakes were synthesized by reacting natural augite crystals in a 1:1 molar ratio of $NaF\text{-}MgF_2$ melt at ~900°C in a platinum crucible (Gregorkiewitz *et al.*, 1974; Gregorkiewitz and Rausell-Colom, 1987). These large flakes, however, are of limited practical value for selective uptake of cations from radioactive and other waste solutions because of their slow diffusion through the interlayer space.

To overcome the slow cation-diffusion problem in large flakes, Paulus *et al.* (1992) developed a synthesis method to manufacture large amounts of phase-pure Na-4-mica with a small and near uniform particle size.

This method utilized a Mg aluminosilicate gel and NaF flux at 890°C. This method, however, is not cost-effective because of the use of expensive chemicals, such as tetraethoxysilane and Al and Mg nitrates, and the method is long and tedious.

To develop a less tedious and cost-effective method, Franklin and Lee (1996) recently reported the development of a simplified "dry-mix and calcine" method using Mg and Al nitrates, fumed silica, and Na fluoride. Komarneni *et al.* (1998) reported the use of metakaolinite as an aluminosilicate source for the economical synthesis of Na-4-mica for several potential applications as indicated above. The objectives of this research were to synthesize Na-4-mica by two different methods using (1) metakaolinite + MgO and (2) Mg aluminosilicate gel and to compare their chemical and particle-size characteristics.

MATERIALS AND METHODS

Synthesis of Na-4-mica samples

Na-4-mica samples were prepared using two different starting precursors, one with metakaolinite and Mg oxide mixture and another with Mg aluminosilicate gel powder. A poorly crystallized kaolinite from Georgia, Clay Minerals Society Source Clay KGa-1, was used as the aluminosilicate source after calcining at 700°C for 18 h. The calcined kaolinite is 'metakaolinite'. The untreated kaolinite has a chemical composition (van Olphen and Fripiat, 1979) of: 43.9 wt. % SiO_2, 38.5 wt. % Al_2O_3, 2.08 wt. % TiO_2, 0.98 wt. % Fe_2O_3, 0.15 wt. % FeO, and 0.03 wt. % MgO.

Metakaolinite and Mg oxide (Ube Industries, Ube, Japan) as the Mg aluminosilicate source (50 wt. %)

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Table 1. Starting compositions, time, and temperature of synthesis and phase formation as determined by XRD using metakaolinite as the aluminosilicate source.

Mica sample number	Starting composition[1]	Treatment time, h at 890°C	Ratio of XRD intensities of hydrated to anhydrous Na-4-mica
Mica-1	Metakaolinite + MgO	24	11.95 Å:9.77 Å ≈ 7:1
Mica-2	Metakaolinite + MgO	24	11.82 Å:9.68 Å ≈ 5:1
Mica-3	Metakaolinite + MgO	24	11.95 Å:9.7 Å ≈ 12:1
Mica-4	Metakaolinite + MgO + 2% extra MgO	24	11.82 Å:9.77 Å ≈ 8:1
Mica-10	Metakaolinite + MgO + 2% extra MgO	24	11.82 Å:9.7 Å ≈ 11:1
Mica-13	Metakaolinite + MgO + 5% extra MgO	24	11.95 Å:9.77 Å ≈ 6:1
Mica-14	Metakaolinite + MgO + 5% extra MgO	24	11.82 Å:9.68 Å ≈ 7:1
Mica-15	Metakaolinite + MgO	12	11.82 Å:9.77 Å ≈ 9:1
Mica-16	Metakaolinite + MgO + 2% extra MgO	12	11.95 Å:9.77 Å ≈ 7:1
Mica-17	Metakaolinite + MgO	6	11.82 Å:9.68 Å ≈ 10:1

[1] 50 wt. % of this starting composition was mixed with 50 wt. % NaF before heat treatment at 890°C.

and NaF (50 wt. %) were mixed and then heated in a Pt crucible at 890°C for different durations (Table 1). The Al:Si ratio in kaolinite was assumed to be 1:1. The Na and F components were in excess whereas the other components were used in stoichiometric amounts; in some cases 2 wt. % excess MgO was used.

The second precursor was a Mg aluminosilicate gel prepared from tetraethoxysilane [$Si(OC_2H_5)_4$] and Mg and Al nitrates as described previously (Paulus et al., 1992). Mg aluminosilicate gel (50 wt. %) and NaF (50 wt. %) were mixed and then heated in a Pt crucible to prepare Na-4-mica at different temperatures (850, 875, and 890°C) for 24 h (Table 2). After heat treatment, the samples were washed with deionized water to remove all soluble salts, followed by saturated boric-acid treatment to remove any fluoride salts insoluble in water. The experimental details of syntheses are described in Paulus (1990), Paulus et al. (1992), and Komarneni et al. (1998). The samples were dried at 60°C and homogenized prior to characterization.

Characterization of samples

Phase purity was determined by powder X-ray diffraction (XRD) on oriented mineral aggregate samples using a Scintag diffractometer with Ni-filtered CuKα radiation. A scan speed of 2°/min was used. Particle morphology was observed in some cases by scanning electron microscopy (SEM) using an ISI-DS130 instrument. ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained at 103.9 and 79.8 MHz respectively using a Varian Unity 400 spectrometer with a double-bearing rotor (5 mm, Zirconia). For ^{27}Al resonance the spectrometer operating conditions were: pulse width 1 μs (measured on an $Al(NO_3)_3$ aqueous solution), spectral width 1 MHz, recycle delay 1 s, 1000 transients and 12 kHz spinning speed. No line broadening was used in data processing. ^{27}Al chemical shifts were measured relative to $Al(H_2O)_6^{3+}$ using aqueous $Al(NO_3)_3$. The Si spectra were obtained by using a 2-μs pulse width, 40 kHz spectral width, recycle delay of 30–90 s, 60 transients, and 8 kHz spinning speed. Line broadening of 40 Hz was used in data processing. ^{29}Si chemical shifts were referenced to the signal of tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Powder XRD results

Table 1 shows the results of all Na-4-mica syntheses from metakaolinite as the aluminosilicate precursor.

Table 2. Starting compositions, temperature, and time of synthesis and phase formation as determined by XRD using magnesium aluminosilicate gel as the precursor.

Mica sample number	Starting composition[1]	Treatment[2] temperature, °C	Ratio of XRD intensities of hydrated to anhydrous Na-4-mica; other phases
Mica-5	Mg aluminosilicate gel	890	12.02 Å:9.77 Å ≈ 2:1
Mica-6	Mg aluminosilicate gel	850	only anhydrous 9.77-Å phase; unidentified peak at 16.98 Å
Mica-9	Mg aluminosilicate gel	875	only anhydrous 9.77-Å phase; unidentified peak at 16.98 Å
Mica-11	Mg aluminosilicate gel + 2 wt. % extra MgO	890	11.95 Å:9.77 Å ≈ 1:2; unidentified peak at 18.77 Å
Mica-12	Mg aluminosilicate gel	890	11.95 Å:9.77 Å ≈ 1:1; very strong peak at 19.11 Å probably superlattice peak of 9.77-Å phase.

[1] 50 wt. % of this gel was mixed with 50 wt. % NaF before heat treatment.
[2] Time of synthesis in all cases was 24 h.
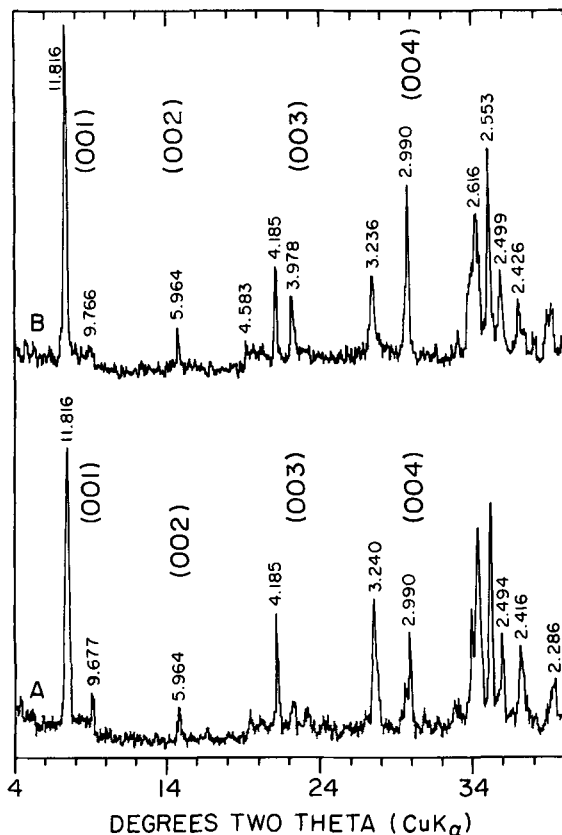
Figure 1. Powder XRD patterns of two Na-4-micas synthesized from metakaolinite as the aluminosilicate source (Table 1): (A) Mica-2 and (B) Mica-15.

Figure 2. Powder XRD patterns of three Na-4-micas synthesized from Mg aluminosilicate gel (Table 2): (A) Mica-5, (B) Mica-6, and (C) Mica-12.

Na-4-mica was obtained in phase-pure form in all cases, *i.e.*, at different durations of 6–24 h at 890°C. In all these syntheses, the predominant form of Na-4-mica was the one-layer hydrate (one layer of water molecules in the interlayer) with a *c* axis spacing in the range of 11.82–11.95 Å (Table 1; Figure 1). Powder XRD clearly shows intense (001) and higher-order (00*l*) reflections of the hydrated phase (Figure 1). There is, however, a small quantity of anhydrous (unhydrated) phase with a *c* axis spacing of 9.68–9.77 Å (Figure 1).

The approximate proportions of one-layer hydrate to anhydrous phase based on X-ray intensity of the 001 reflection are given in Table 1. The reason for a small portion of the Na-4-mica to remain unhydrated is not clear but may be due to the presence of a small amount of glassy phase on the edges of the particles which prevented hydration of the interlayer cations (see SEM results below). The full-width at half-height (FWHH) of the ^{29}Si MAS NMR signals also suggests the presence of a glassy phase (see below). For applications involving cation exchange, a higher proportion of the hydrated phase is preferred because exchange is unlikely for the anhydrous phase.
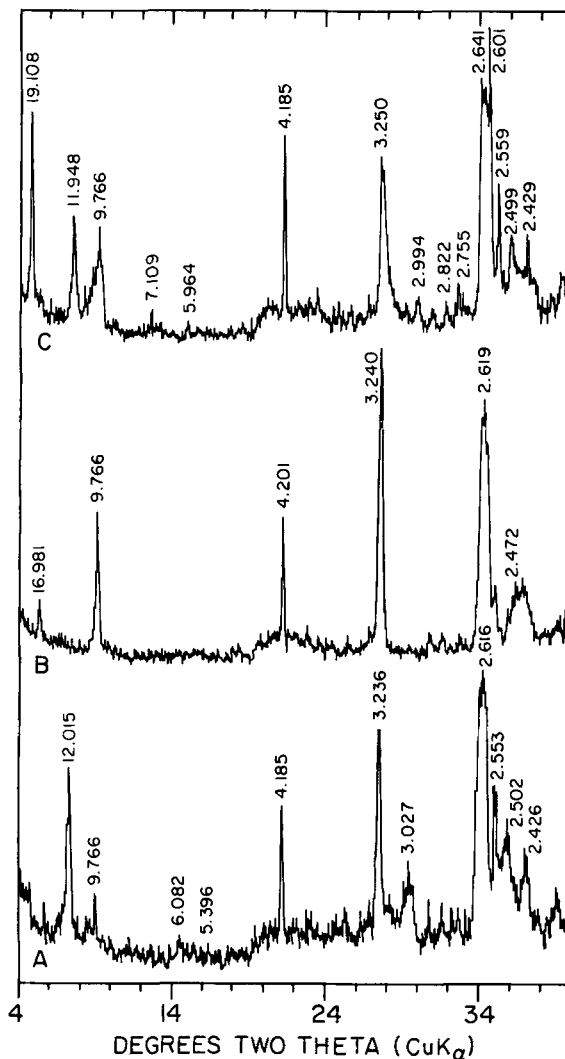
Table 2 shows the synthesis results for all Na-4-micas from Mg aluminosilicate gel precursor. Na-4-mica was synthesized in all cases, but the anhydrous form predominated in most experiments (Table 2). At temperatures of 850 and 875°C, only the anhydrous phase was observed. The significance of temperature needs further investigation. Similar results were also obtained by Franklin and Lee (1996). Powder XRD results of three Na-4-micas prepared from Mg aluminosilicate gels are given in Figure 2. The XRD results show the presence of hydrated and anhydrous phases in Mica-5 (Figure 2A), an anhydrous phase in Mica-6 with an unidentified peak at 16.98 Å (Figure 2B), and both hydrated and anhydrous phases in equal amounts in Mica-12. In addition, Mica-12 has a peak of 19.11 Å which is apparently the superlattice peak of the an-
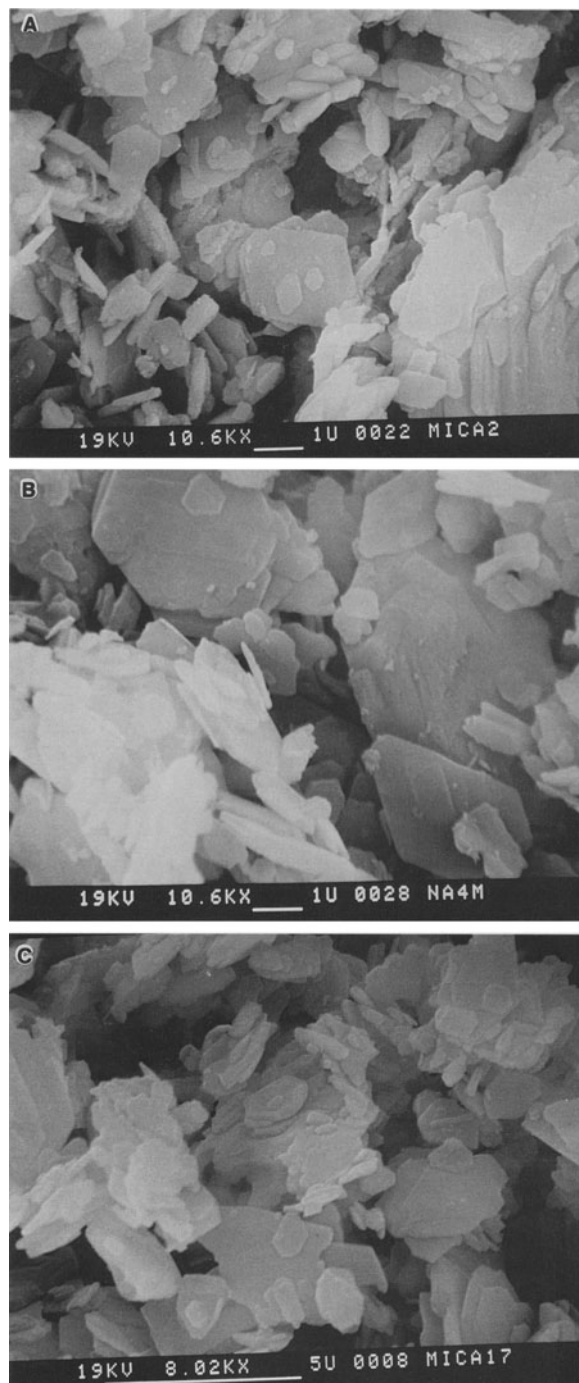
Figure 3. SEM micrographs of Na-4-micas synthesized from metakaolinite as the aluminosilicate source at 890°C for different durations (Table 1): (A) Mica-2, (B) Mica-15, and (C) Mica-17.

tern of Na-4-mica and further XRD characterization is necessary.

The predominant presence of an anhydrous phase in the Na-4-mica samples prepared from a gel precursor at 850–875°C makes these samples unsuitable for cation exchange applications. In general, synthesis from the kaolinite precursor yielded greater amounts of Na-4-mica products than from a Mg aluminosilicate gel precursor (Tables 1 and 2). Thus, preparation of Na-4-mica from inexpensive kaolinite is expected to be cost effective. Precise control of synthesis conditions is necessary to obtain nearly completely hydrated Na-4-mica from a Mg aluminosilicate gel (Paulus et al., 1992), while it is not a strict requirement when metakaolinite is the aluminosilicate source.

Particle size and morphology

SEM micrographs of Na-4-micas synthesized from the metakaolinite precursor are given in Figure 3. Particle size ranges between 1–5 μm, and the plate-like particles have pseudohexagonal morphology. No significant differences in particle size were observed for Na-4-mica samples prepared at 890°C for 6–24 h (Figure 3). Further reduction to submicrometer size is required for effective use of Na-4-mica in cation-exchange applications. SEM micrographs of two Na-4-micas synthesized from Mg aluminosilicate gel are given in Figure 4. These micas show massive structure (Figure 4A and 4C) unlike those prepared from metakaolinite (Figure 3) with the hexagonal clay mineral particles being sintered together (Figure 4B and 4D) probably by a glassy phase. Mica-6, which only showed anhydrous phases by XRD, clearly reveals that the hexagonal flakes are not well differentiated, i.e., they are sintered together (Figure 4B) and this is probably why they did not hydrate. Na-4 micas synthesized from kaolinite, on the other hand, showed mainly discrete clay particles and therefore were hydrated (Figure 2; Table 1).

^{27}Al and ^{29}Si MAS NMR spectroscopy

^{27}Al and ^{29}Si MAS NMR results for several synthetic Na-4-micas are summarized in Table 3. The ^{27}Al MAS NMR results clearly show that Al is mostly present in tetrahedral coordination. However a minor amount of Al is present also in octahedral coordination in most samples. The use of excess MgO, i.e., more than the stoichiometric amount, in synthetic mica samples 4, 13, and 14, did not eliminate octahedral Al. The presence of Al creates excess positive charge in the octahedral sheet and hence is expected to reduce the overall charge of the 2:1 layer. Typical ^{27}Al MAS NMR spectra of two Na-4-mica samples, one prepared from metakaolinite plus MgO and another from Mg aluminosilicate gel, are shown in Figure 5. One of these samples (Figure 5B) shows the presence of a small amount of octahedral Al. Further optimization

hydrous mica with a *d*-value of 9.77 Å (Figure 2C). The peaks at ~4.185 and 2.553 Å may be due to cristobalite. All the XRD peaks are not identified because we have not been able to index the powder XRD pat-
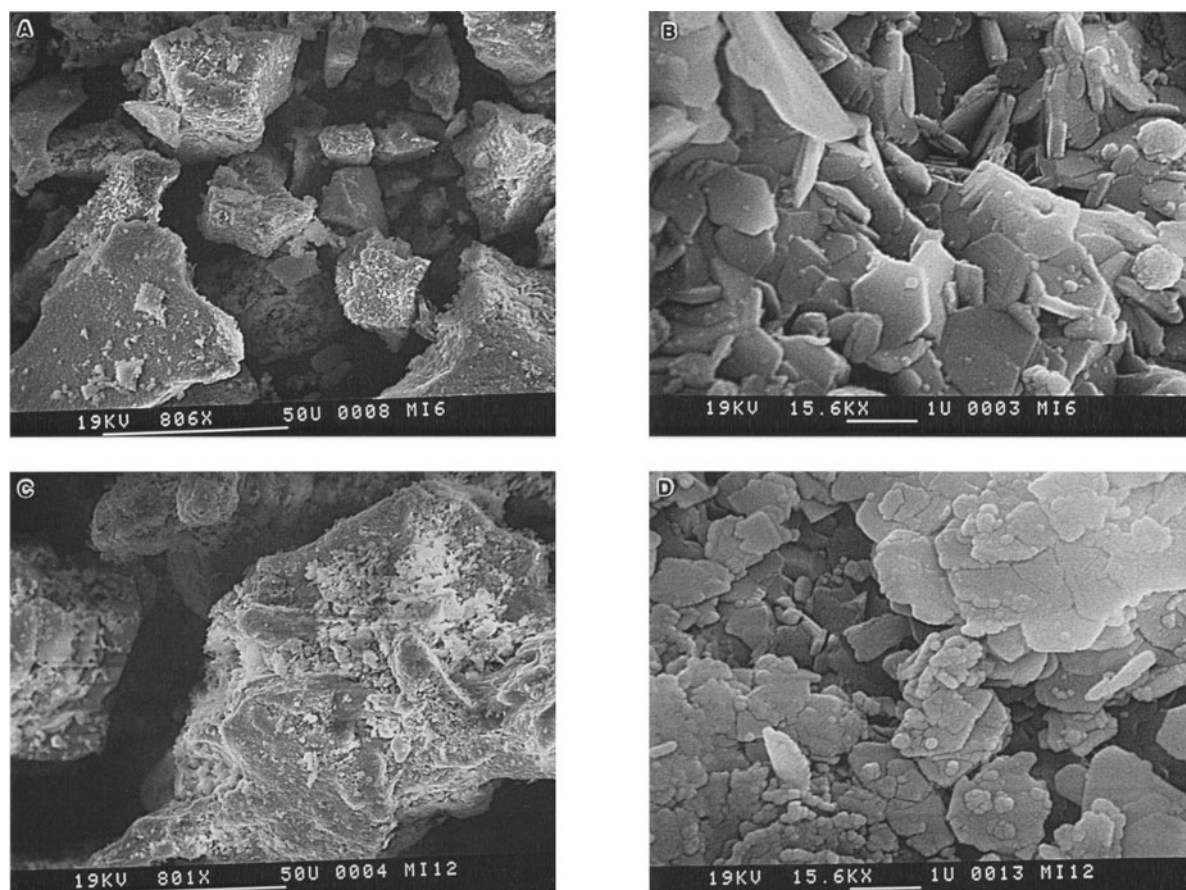
Figure 4. SEM micrographs of Na-4-micas synthesized from Mg aluminosilicate gel at two different temperatures (Table 2): (A) Mica-6 at low magnification showing massive grains, (B) same as (A) but at higher magnification showing undifferentiated (sintered) hexagonal plates, (C) Mica-12 at low magnification showing massive grains, and (D) same as (C) but higher magnification showing agglomerated small particles.

Table 3. ^{27}Al and ^{29}Si MAS NMR spectroscopy results of several synthetic Na-4-mica samples.

Na-4-Mica sample number	^{27}Al resonances, ppm from $[Al(H_2O)_6]^{3+}$		^{29}Si resonances, ppm from tetramethylsilane in order of intensity
	Tetra-hedral	Octahedral	
Mica-1	68.2	−0.5	−74.7; −77.1; −70.7; −81.3
Mica-4	68.5	−0.8	−77.5; −75.0; −80.1; −71.0; −81.6
Mica-5	69.4[1]	0.2	−74.7; −77.3; −81.3
Mica-6	69.7[1]	None	−74.7; −78.3; −81.3
Mica-11	69.4[1]	None	−74.8; −77.2
Mica-12	69.4[1]	−0.1	−74.8; −77.2; −80.9
Mica-13	67.9	−0.2	−77.0; −74.6; −80.1; −81.6; −82.4; −70.9
Mica-14	68.2	−0.3	−77.2; −74.9; −79.3; −71.2
Mica-15	67.9	−0.3	−77.2; −75.0
Mica-17	67.9	−0.4	−77.3; −75.6; −81.1

[1] ^{27}Al spectra of these samples show a shoulder near 65 ppm representing a second Al tetrahedral environment probably of the glassy phase.

of the synthesis procedure may eliminate the octahedral Al completely to achieve maximum cation exchange capacity. The Na-4 mica samples prepared from a gel precursor showed a shoulder (Figure 5A) near 65 ppm (Table 1) which represents a second tetrahedral Al environment (Figure 4).

^{29}Si MAS NMR results clearly show the presence of two Si(3Al) resonances (Tables 3 and 4) representing two types of ^{IV}Si environments. The fully anhydrous Mica-6 shows predominantly a resonance at −74.7 ppm with a minor resonance at −78.3 ppm (Figure 6A). One of the more hydrated samples (Mica-17, see Table 1), on the other hand, shows a predominant resonance at −77.3 ppm with a significant resonance at −75.6 ppm (Figure 6B). However, we do not understand the nature of these two Si(3Al) environments. We note, however, that small changes in the chemical shifts of resonances corresponding to the same tetrahedral environment were previously attributed to differences in the octahedral and interlayer environment of Si (Sanz and Serratosa, 1984).
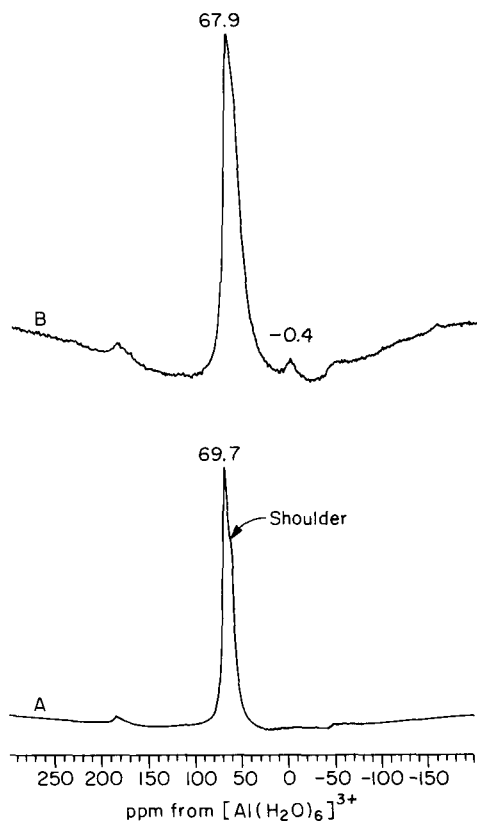
Figure 5. ^{27}Al MAS NMR spectra of Na-4-micas: (A) Mica-6 synthesized using Mg aluminosilicate gel (Table 2) showing a shoulder on the 69.7 ppm resonance and (B) Mica-17 synthesized using metakaolinite as the aluminosilicate source (Table 1).

Figure 6. ^{29}Si MAS NMR spectra of Na-4-micas: (A) Mica-6 (Table 2) and (B) Mica-17 (Table 1).

All synthetic micas show minor resonances (Table 1; Figure 6) in the range of -80.1 to -82.4 ppm which may be attributed to Si(2Al) environments based on Herrero *et al.* (1987) and Komarneni *et al.* (1998). In a few synthetic micas (Table 3), a minor resonance in the range of -70.7 to -71.2 ppm was observed which
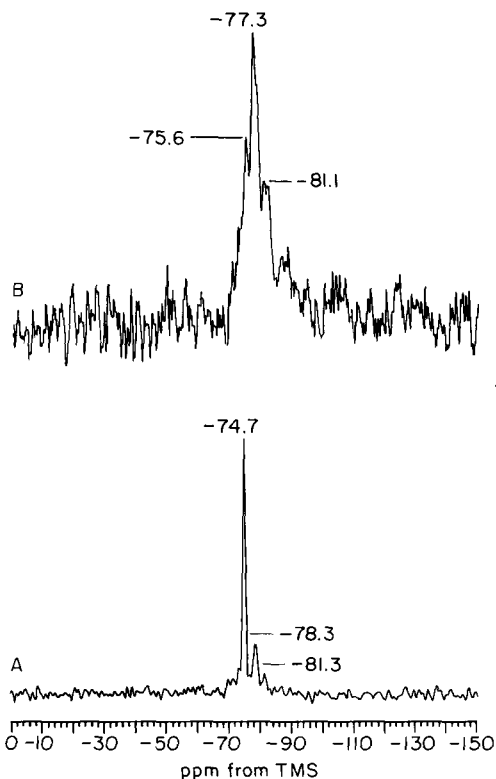
cannot be assigned to a specific environment. The assignments of all ^{29}Si resonances to various environments are summarized in Table 4. These results show that all the synthetic micas exhibited mainly Si(3Al) environments as expected in a completely ordered Na-4-mica with a Si:Al ratio 1:1 in the tetrahedral sheet (Kinsey *et al.*, 1985). The widths of the ^{29}Si MAS NMR signals of these synthetic micas suggest that a glassy phase is present with the crystalline micas. This result is consistent with SEM and ^{27}Al MAS NMR

Table 4. Assignment of ^{29}Si resonances based on previous studies (Sanz and Serretosa, 1984; Kinsey *et al.*, 1985).

Mica sample	Assignment of ^{29}Si resonances					
	Unknown	Q3(3Al)	Q3(3Al)	Q3(2Al)	Q3(2Al)	Q3(2Al)
Metakaolinite + MgO						
Mica-1	-70.7	-74.7	-77.1		-81.3	
Mica-4	-71.0	-75.0	-77.5	-80.1	-81.6	
Mica-13	-70.9	-74.6	-77.0	-80.1	-81.6	-82.4
Mica-14	-71.2	-74.9	-77.2	-79.3		
Mica-15		-75.0	-77.2			
Mica-17		-75.6	-77.3		-81.1	
Mg aluminosilicate gel						
Mica-5		-74.7	-77.3		-81.3	
Mica-6		-74.7	-78.3		-81.3	
Mica-11		-74.8	-77.2			
Mica-12		-74.8	-77.2			

data. However, further studies are required to determine why some Na-4-mica remains unhydrated.

CONCLUSIONS

Metakaolinite was found to be a good aluminosilicate source in the synthesis of the hydrated Na-4-mica, with an ideal Si:Al ratio of 1:1 in the tetrahedral sheet. The synthesis of Na-4-mica using metakaolinite is expected to be cost-effective because this precursor is an inexpensive source of Si:Al in a 1:1 ratio. ^{27}Al and ^{29}Si MAS NMR spectra confirmed the expected coordination and arrangement of Al and Si in synthesized Na-4-micas.

ACKNOWLEDGMENTS

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