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LETTER

Observation of five-coordinated Al in pyrophyllite dehydroxylate by solid-state ^{27}Al NMR spectroscopy at 14 T

JOHN J. FITZGERALD
Department of Chemistry, South Dakota State University, Brookings, South Dakota 57007, U.S.A.
STEVEN F. DEC
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, U.S.A.
ABDULLATEF I. HAMZA
Department of Materials Engineering and Science, South Dakota School of Mines and Technology,
Rapid City, South Dakota 57701, U.S.A.

ABSTRACT

The observation and quantification of four-, five-, and six-coordinated Al sites in Al-containing materials such as silica-aluminas, transition aluminas, and clay-derived solids are major problems in solid-state ^{27}Al NMR spectroscopy. We report herein solid-state ^{27}Al NMR spectra of the mineral derivative pyrophyllite dehydroxylate; these spectra were obtained at 14 T (the highest available magnetic field), 11.7 T, and 8.4 T under high-speed (>12 kHz) magic-angle sample-spinning (MASS) conditions. The results represent the first observation of the $^{[5]}$Al site in this mineral derivative. The ^{27}Al MASS NMR spectrum at 14 T demonstrates the advantage of high-field NMR measurements for observing the signal due to this highly distorted $^{[5]}$Al site. The NMR spectra and computer simulations were used to determine the isotropic chemical shift (29 ppm), quadrupolar coupling constant (10.5 MHz), and asymmetry parameter ($\eta = 0.6$) for the Al atom in the trigonal-bipyramidal Al-O local environment of this mineral derivative. These high-resolution ^{27}Al MASS NMR results provide impetus for future solid-state NMR studies of important Al-containing catalysts, ceramic precursors, and other solid oxide materials containing quadrupolar nuclides amenable to solid-state NMR.

INTRODUCTION

^{27}Al is the most thoroughly studied quadrupolar nuclide in solid-state NMR spectroscopy. Its applicability to crystalline and amorphous inorganic materials such as zeolites (Klinowski, 1984; Thomas and Klinowski, 1985), oxide catalysts (John et al., 1983), glasses (Kirkpatrick et al., 1986), ceramics (Turner et al., 1987), clays (Kinsey et al., 1985), and clay-derived materials (Fitzgerald et al., 1989; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987) has been extensively explored. A major feature of solid-state ^{27}Al NMR has been the notable variation of the chemical shift of the central transition (½, −½) resonance with local Al coordination, particularly for 4-coordinated and 6-coordinated Al-O sites (Muller et al., 1986). Since the early work of Mueller et al. (1981), solid-state ^{27}Al NMR has been widely used qualitatively, and in some cases quantitatively (Fitzgerald et al., 1989), to determine the relative content of octahedral ($^{[6]}$Al) and tetrahedral ($^{[4]}$Al) aluminum. $^{[6]}$Al yields isotropic chemical shifts between −10 and 20 ppm, and those of $^{[4]}$Al are between 50 and 80 ppm (Muller et al., 1986). Although detection of $^{[4]}$Al and $^{[6]}$Al is usually easy at high magnetic fields and magic-angle sample-spinning (MASS), quantitation of relative site occupancy is often complicated by second-order quadrupolar line-broadening and the potential loss of signal because of spinning sidebands (Fitzgerald et al., 1989; John et al., 1983; Muller et al., 1986; Thompson et al., 1987; Turner et al., 1987). The spinning sidebands introduce signal intensity between the $^{[4]}$Al and $^{[6]}$Al resonances, but this problem has been largely overcome by rapid sample spinning at greater than 12 kHz (Dec et al., 1986; Fitzgerald et al., 1989).

In many cases, the effects of the second-order quadrupolar interaction are more serious. Quadrupolar line-broadening is characterized by the quadrupole coupling constant (qcc), e^2qQ/h, a measure of the interaction of the nuclear quadrupolar moment (eQ) with the electric-field gradient at the nucleus (eq). If qcc is large, the ^{27}Al NMR peak for a given structural site can be broadened, displaced to values more shielded than the true (isotropic)

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chemical shift, and split and distorted into complicated line-shapes (Muller et al., 1986; Thompson et al., 1987). For a given qcc, the second-order broadening effects (observed line-widths and line-shapes) decrease as the magnetic-field strength increases, but are still influenced by the asymmetry of the electric-field gradient, described by the asymmetry parameter, η, which is a measure of the deviation of the electric field of the nucleus from cylindrical symmetry.

For most $^{[4]}$Al and $^{[6]}$Al sites even with large qcc, ^{27}Al NMR measurements at high magnetic fields (e.g., 11.7 and 14.0 T) minimize second-order line-broadening and permit observation of the true line-shape and position of the resonances (Fitzgerald et al., 1989; Muller et al., 1986; Thompson et al., 1987). Some five-coordinated ($^{[5]}$Al) sites have also been observed (Alemany and Kirker, 1986; Cruickshank et al., 1986).

Quantitative determination of Al-O sites of different coordination and apparently low symmetry in transition aluminas (John et al., 1983), silica-aluminas (Gilson et al., 1987), and Si-Al clay-derived materials (Dec and Maciel, unpublished results, 1989; Fitzgerald et al., 1989; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987) by ^{27}Al NMR has been difficult. Transition aluminas (John et al., 1983) yield two resonances assigned to $^{[4]}$Al and $^{[6]}$Al, but from a site-symmetry viewpoint, these signals are poorly quantified and understood. Some materials also yield a weak ^{27}Al NMR signal in the 30 to 45 ppm range that is due to either highly distorted $^{[4]}$Al sites or $^{[5]}$Al sites (Dec and Maciel, unpublished results, 1989). Recent studies of aluminates such as barium-aluminum glycolate (Cruickshank and Dent Glasser, 1985a, 1985b; Cruickshank et al., 1986), dehydrated kaolin intermediates (Fitzgerald et al., 1989; Gilson et al., 1987; Lambert et al., 1989; MacKenzie et al., 1985b; Meinhold et al., 1985; Watanabe et al., 1987), and hydrothermally dealuminated faujasite, ZSM-5 and Al_2O_3-SiO_2 gels (Gilson et al., 1987) have also reported the presence of signals for a range of $^{[4]}$Al, $^{[5]}$Al, and $^{[6]}$Al. ^{27}Al NMR signals in the range of 31 to 37 ppm have been commonly assigned to $^{[5]}$Al on the basis of ^{27}Al NMR data observed for known $^{[5]}$Al sites contained in andalusite at 35 to 36 ppm (Alemany and Kirker, 1986; Lippmaa et al., 1986) and barium-aluminum glycolate at 36 ppm (Cruickshank et al., 1986). Quantitation of the relative content of the three ^{27}Al NMR resonances in treated clays, Al_2O_3-SiO_2 gels, and zeolites has been particularly difficult even at 9.4 T and 6-kHz MASS speeds because of incomplete averaging of the second-order quadrupolar broadening.

The experimental difficulties in completely or even partially observing 5-coordinated ($^{[5]}$Al) resonances in Al-containing solids is most exemplified by recent ^{27}Al NMR studies of heated and dehydrated kaolin and pyrophyllite (Fitzgerald et al., 1989; Frost and Barron, 1984; Lambert et al., 1989; MacKenzie et al., 1985a, 1985b; Meinhold et al., 1985; Watanabe et al., 1987). Pyrophyllite is a dioctahedral 2:1 phyllosilicate [$Al_4Si_8O_{20}(OH)_4$] (Bailey, 1966; Rayner and Brown, 1966; Wardle, 1972; Wardle and Brindley, 1972). On heating, it loses its hydroxyl water from about 550 to 900 °C, forming pyrophyllite dehydroxylate that shows a distinct X-ray pattern characteristic of the presence of $^{[5]}$Al with approximately trigonal-bipyramidal symmetry (Rayner and Brown, 1966; Wardle, 1972). Recent solid-state ^{29}Si and ^{27}Al NMR studies (Frost and Barron, 1984; MacKenzie et al., 1985a) of the thermal dehydroxylation of pyrophyllite have shown limited changes in the ^{29}Si NMR chemical shifts but drastic changes in the ^{27}Al NMR spectra including a 90% loss of the ^{27}Al NMR signal intensity. The $^{[5]}$Al signal of pyrophyllite dehydroxylate has to date been unobservable owing to substantial second-order quadrupolar line-broadening.

We report here solid-state ^{27}Al NMR spectra of pyrophyllite and pyrophyllite dehydroxylate at 14 T (the highest available magnetic field) under magic-angle sample-spinning (MASS) conditions that clearly show the $^{[5]}$Al resonance in the dehydroxylate. The observation of this $^{[5]}$Al resonance indicates the likely success for future studies of other hydroxylated minerals such as kaolin, muscovite, and montmorillonite, which have been proposed to contain $^{[5]}$Al in their dehydroxylated derivatives.

EXPERIMENTAL DETAILS

The pyrophyllite was obtained from the D. J. Mineral Kit Company, P.O. Box 761, Butte, Montana, U.S.A. (lot M-260, a natural deposit in Nevada). The mineral specimen was gently crushed, sieved through a 60–80 mesh screen, and hand-picked microscopically. Pyrophyllite dehydroxylate was obtained by heating white, fibrous, powdered pyrophyllite in a muffle furnace at 550 °C for 7 d. The fluffy fibrous powder showed X-ray diffraction patterns identical to those reported by Wardle (1972) and Wardle and Brindley (1972), with minor diffraction peaks due to unreacted pyrophyllite.

^{27}Al MASS NMR spectra were recorded on a modified Nicolet NT-360 NMR spectrometer and on Bruker AM-500 and AM-600 NMR spectrometers, using home-built probes. MASS speeds of 11.0–12.0 kHz were obtained using 6.0-mm (outer diameter) Torlon spinners on the NT-360 spectrometer. MASS speeds of 16–17 kHz were obtained using 4.5-mm (outer diameter) Torlon spinners on the AM-500 and AM-600 spectrometers. The chemical-shift reference (by sample substitution) was an aqueous solution of 1 M $AlCl_3 \cdot 6H_2O$, which was assigned a chemical shift value of 0.0 ppm. Higher chemical shifts correspond to larger resonance frequencies and lower shielding constants. ^{27}Al 90° pulses for 1 M $AlCl_3$ (aqueous) were 8.5, 6.5, and 6.0 μs at 93.8, 130.3, and 156.4 MHz, respectively. ^{27}Al pulse lengths of 1.3, 0.5, and 0.5 μs were used at 93.8, 130.3, and 156.4 MHz, respectively, with recorded spectra being obtained using 50-ms relaxation delays.

X-ray powder-diffraction analyses of pyrophyllite and its heated derivatives were obtained using a Phillips-Norelco diffractometer equipped with a graphite monochrometer, a Cu$K\alpha$ X-ray source at 1.5418 Å, and a Dynamaster 64A recorder over the 2θ range 1° to 45°.

RESULTS AND DISCUSSION

The ^{27}Al MASS NMR spectrum of pyrophyllite at 14 T shows a single sharp resonance at 4.3 ppm (not shown)

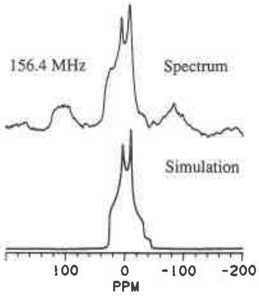

Fig. 1. Solid-state ^{27}Al NMR spectrum of pyrophyllite dehydroxylate at 14 T (156.4 MHz) under 16.0-kHz MASS conditions; (upper) experimental and (lower) computer-simulated spectra.

in agreement with previous studies (Frost and Barron, 1984; Kinsey et al., 1985; MacKenzie et al., 1985a). Pyrophyllite dehydroxylate was produced by heating powdered, fibrous pyrophyllite at 550 °C for 7 d to produce a fluffy fibrous powder with an X-ray powder-diffraction pattern similar to that of Wardle and Brindley (1972). The ^{27}Al MASS NMR spectrum of pyrophyllite dehydroxylate at $\mathbf{H}_0 = 14$ T (156.4-MHz) and 16-kHz sample spinning is shown in Figure 1 (upper) together with the computer-simulated spectrum (lower) obtained using the NMR simulation program by Dennis Hare. Simulated spectra were calculated at qcc values of 9.5 to 11.0 MHz and η values of 0.0 to 1.0 with 200-Hz exponential line-broadening. The best-fit simulated spectrum (Fig. 1, lower) had an isotropic chemical shift of 29 ppm at qcc = 10.5 MHz and $\eta = 0.6$. These parameters indicate that the observed Al in the sample is in a 5-coordinated site and has a large electric-field gradient and that the $^{[5]}$Al site is highly distorted. These $^{[5]}$Al resonance parameters are comparable to those of the $^{[5]}$Al sites in andalusite (35–36 ppm, qcc = 5.9 MHz, $\eta = 0.69$–0.70) and barium-aluminum glycolate (35.3–37 ppm, qcc and η undetermined) (Alemany and Kirker, 1986; Cruickshank et al., 1986; Lippmaa et al., 1986). Previous solid-state ^{27}Al NMR studies of pyrophyllite dehydroxylate and other dehydrated pyrophyllite intermediates at lower fields and lower sample-spinning speeds have been unsuccessful primarily owing to the qcc value of the Al site in this material.

Comparisons of the ^{27}Al NMR spectra of our pyrophyllite dehydroxylate at $\mathbf{H}_0 = 14$ T (156.4 MHz), 11.4 T (130.3 MHz), and 8.4 T (93.8 MHz) as shown in Figure 2 illustrate the advantages of higher fields and rapid MASS conditions. The 14- and 11.4-T spectra both show the $^{[5]}$Al signal, although even at 11.4 T, substantial second-order quadrupole effects preclude detailed analysis and determination of the qcc and η parameters of this $^{[5]}$Al site resonance. The spectrum taken at 8.4 T shows the presence of only $^{[6]}$Al, apparently because of a small amount of undehydroxylated pyrophyllite as confirmed by the XRD analysis. The complete absence of the resonance due to the $^{[5]}$Al at this field is consistent with previous studies at lower magnetic fields (Frost and Barron, 1984; MacKenzie et al., 1985a).

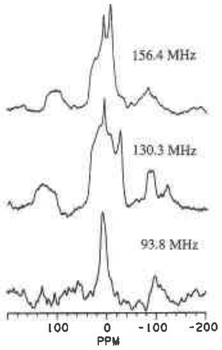

Fig. 2. Solid-state ^{27}Al NMR spectra of pyrophyllite dehydroxylate at various magnetic fields and MASS conditions; (upper) 14 T and 156.4 MHz, (middle) 11.7 T and 130.3 MHz, and (lower) 8.4 T and 93.8 MHz.

This study of the ^{27}Al NMR spectrum of thermally produced pyrophyllite dehydroxylate provides a number of important observations: (1) the isotropic chemical shift and second-order powder pattern of the central $(\frac{1}{2}, -\frac{1}{2})$ transition of the observed resonance is consistent with its assignment to a $^{[5]}$Al site similar to that of andalusite and barium-aluminum glycolate (Alemany and Kirker, 1986; Cruickshank et al., 1986; Lippmaa et al., 1986); (2) highly distorted $^{[5]}$Al sites with large qcc and lower η parameters require the highest available magnetic fields to narrow the unsymmetrical powder patterns caused by the large qcc line-broadening effects; (3) rapid (>12 kHz) MASS conditions are needed to decrease the intensity of spinning sidebands from the region of spectral interest; and (4) similar solid-state ^{27}Al NMR studies at $\mathbf{H}_0 = 14$ T (156.4 MHz) of other clay-derived materials are likely to be an important approach to obtain quantitative $^{[4]}$Al, $^{[5]}$Al, and $^{[6]}$Al site contents in various Al-containing materials. Experimental solid-state ^{27}Al NMR studies of various clay-derived and Al-containinng solids of importance as inorganic catalysts and advanced materials are in progress.

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