

Determination of ^{27}Al Quadrupolar Coupling Parameters and of Metallic Aluminium in Commercial Lithium Aluminium Hydride by ^{27}Al MAS NMR

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The ^{27}Al quadrupolar coupling parameters ($C_Q = 3.90$ MHz and $\eta = 0.30$) and a high content of metallic aluminium (16 ± 2 atom %) have been determined for commercial LiAlH_4 using ^{27}Al MAS NMR spectroscopy.

During the course of an investigation on cross-polarization (CP) dynamics for the ^{27}Al quadrupolar nucleus we have shown that the optimum CP conditions depend strongly on the quadrupolar coupling constant (C_Q) and on the employed spinning speed.¹ Unsuccessful attempts to observe $^{27}\text{Al}\{^1\text{H}\}$ CP/MAS NMR spectra for LiAlH_4 , an expected suitable set-up sample for $^{27}\text{Al}\{^1\text{H}\}$ CP/MAS NMR, have recently been reported in the exploratory ^{27}Al CP study by Morris and Ellis.² Thus, a knowledge of the ^{27}Al C_Q -parameters for LiAlH_4 is of interest.

This communication reports on the determination of the ^{27}Al quadrupolar coupling parameters and on the detection of rather large quantities of metallic Al in commercial LiAlH_4 using ^{27}Al MAS NMR. A standard ^{27}Al MAS NMR spectrum recorded using a 100 kHz spectral window and high-power proton decoupling is shown in Fig. 1. Without proton decoupling the spectrum is severely broadened by ^{27}Al - ^1H heteronuclear dipolar couplings. For the central ($m = +1/2 \leftrightarrow m = -1/2$) transition we observe a characteristic second-order quadrupolar broadened lineshape³ in the typical ^{27}Al chemical shift region from 50 to 100 ppm for tetrahedral Al (Fig. 1a). Simulation of this lineshape at two different

magnetic field strengths, 9.4 and 7.1 Tesla (Fig. 1b and c), gives the best values for $C_Q = 3.90 \pm 0.05$ MHz, the asymmetry parameter $\eta = 0.30 \pm 0.05$, and $\delta(^{27}\text{Al}) = 102.0 \pm 0.5$ ppm. The chemical shift is in good agreement with the value $\delta = 101$ ppm reported for a solution of LiAlH_4 in ether.⁴ The outer satellite transitions ($m = \pm 3/2 \leftrightarrow m = \pm 1/2$ and $m = \pm 5/2 \leftrightarrow m = \pm 3/2$) are responsible for the series of weak spinning sidebands (ssbs), that extend over the entire 100 kHz spectral window. Recently we have shown that the complete envelope of ssb intensities for these transitions depends on the C_Q and η values, and that these parameters can be determined from computer simulation of the ssb manifold.⁵ Thus, to verify independently the values determined for C_Q and η , the spectral window was increased from 0.1 to 1.0 MHz for observation of the full frequency range of the ssbs. The simulated ssb spectrum (not shown), obtained using the quadrupolar coupling parameters determined above, is in excellent agreement with the experimental spectrum.

In addition to the observation of the entire ssb manifold for LiAlH_4 another strong resonance appeared (somewhat to our surprise) at 1639.5 ppm (Fig. 2), *i.e.* far outside the normal ^{27}Al chemical shift region. The lack of ssbs from the satellite

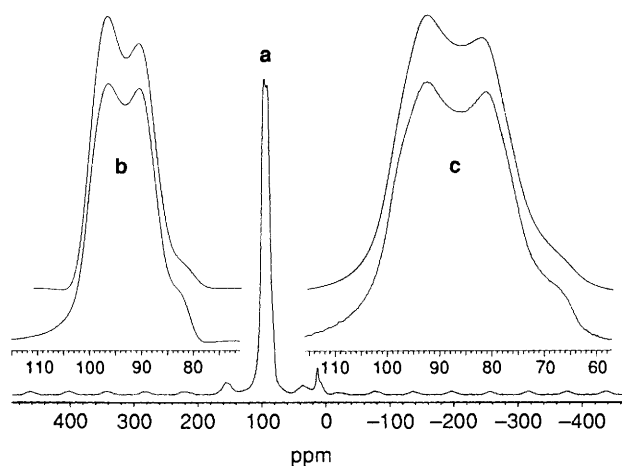


Fig. 1 ^{27}Al MAS NMR spectra of commercial LiAlH_4 . (a) Spectrum recorded at 9.4 T using a 100 kHz spectral width and spinning speed of 6330 Hz; the low-intensity resonance observed at ca. 12 ppm is most likely a product of hydrolysis. (b) Expansion of the central transition in (a) showing experimental (lower) and simulated (upper) spectra; to resolve the doublet splitting at 9.4 T, a slight gaussian/lorentzian resolution enhancement was applied to the FIDs. (c) 7.1 T spectrum of the central transition (no linebroadening) for comparison of experimental (lower) and simulated (upper) spectra. The simulated spectra in (b) and (c) both correspond to $C_Q = 3.90$ MHz and $\eta = 0.30$. Note the increased quadrupolar line broadening in the 7.1 T spectrum (c)

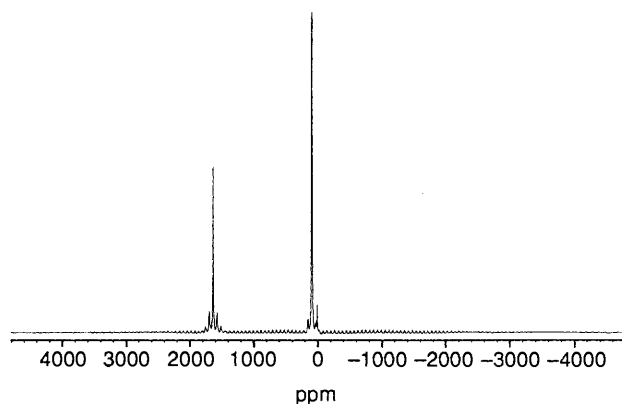


Fig. 2 ^{27}Al MAS NMR spectrum of commercial LiAlH_4 recorded at 9.4 T (Varian VXR-400 S spectrometer) using a 1.0 MHz spectral width, spinning speed of 6330 Hz, and on-resonance condition for the LiAlH_4 resonance. The resonance at 1639.5 ppm is that of metallic aluminium

transitions for this resonance indicates zero or negligible electric field gradients at the sites of the ^{27}Al nuclei. The huge shift to higher frequency (downfield) of this resonance must be caused by an interaction which is at least an order of magnitude larger than the one responsible for the chemical shifts. For metallic compounds the conduction electrons cause large high-frequency shifts, the so-called Knight shift. Thus, the 1640 ppm resonance has been assigned to that of metallic aluminium as confirmed by independently recording the ^{27}Al MAS spectrum of finely divided Al-powder packed in a Si_3N_4 rotor and also in perfect agreement with the work of Andrew *et al.*⁶

Since LiAlH_4 is an important reagent in organic synthesis, it is of interest to quantify the content of metallic aluminium by

^{27}Al MAS NMR. However, this requires special experimental and theoretical considerations. To obtain reliable relative signal intensities from Al-sites with different quadrupolar couplings very strong rf field strengths, $\gamma H_1/2\pi$, and short pulse widths, $(I + 1/2)(\gamma H_1/2\pi)t_p \leq 1/12$, must be applied experimentally.⁷ Furthermore, because of the huge off-resonance effects, for at least one of the two Al-sites, two separate spectra with on-resonance condition (including proper probe tuning) for each site and otherwise identical parameters were recorded. To ensure full relaxation of both resonances, a recycle delay of 32 s was employed (determined from an experiment of arrayed recycle delays).

The cubic structure of metallic Al and thus its vanishing quadrupolar coupling leads to degeneracy for the five ^{27}Al transitions for this species. Therefore, integration of this resonance, including its few sidebands (total of six), gives the total signal intensity, I_{total} , for all five transitions. For LiAlH_4 we are concerned with integration of the signal intensity for the central (+1/2, -1/2) transition only. For ideal excitation the contribution of the individual transitions to I_{total} is given by eqn. (1) where $I_{m,m-1}$ is the intensity of the $m,m-1$ transition and K is a constant. From eqn. (1), eqn. (2) follows.

$$I_{m,m-1} = K[I(I+1) - m(m-1)] \quad (1)$$

$$I_{\text{total}} \equiv \sum I_{m,m-1} = (35/9)I_{\text{central}} \quad (2)$$

Careful integration of I_{total} and I_{central} for the metallic Al and LiAlH_4 resonances, respectively (excluding contributions from possible overlap of the satellite transitions ssbs but including appropriate sidebands from the LiAlH_4 central transition), and using eqn. (2) shows that the content of metallic aluminium is $16 \pm 2\%$ (atom % Al) for our sample. The presence of metallic Al as an impurity in LiAlH_4 is not surprising considering the preparative method.⁸ However, the supplier claims a LiAlH_4 purity of at least 98% based on a gas-volumetric analysis. We conclude that proper use of ^{27}Al MAS NMR techniques, as outlined here, represents the most direct and convenient method for determining the content of metallic aluminium in LiAlH_4 . Most other methods (*e.g.* XRF, AAS, PIXE, and PIGE) are incapable of distinguishing different Al species in a sample. Finally, the large quantity of metallic Al obviously has important impacts on the quantitative use of LiAlH_4 as a reagent in organic synthesis.

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