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^{27}Al NMR spectroscopy at multiple magnetic fields and ab initio quantum modeling for kaolinite

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Abstract

Diffraction methods indicate clearly that there are two crystallographic Al sites in kaolinite with different site symmetry. Many unsuccessful attempts have been made to resolve the two different Al sites in kaolinite by magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy since the early 1980s. This study attempts to resolve these sites, derive accurate quadrupolar coupling parameters at the two sites, and explain the reasons for the lack of separation by combining NMR spectroscopy at various fields with ab initio quantum modeling.

At a high field such as 21.06 T, large chemical shift anisotropy and dipolar effects can overwhelm the quadrupolar interaction effects for sites with relatively small C_q values such as the two Al sites in kaolinite. The spectra will then display featureless lineshapes lacking the typical quadrupolar interaction characteristics. At lower fields, such as 4.68 T, the quadrupolar interaction effects become dominant, but due to the similarity of the two Al environments in kaolinite, as well as broadening by residual dipole-dipole and chemical shift anisotropy, the ^{27}Al MAS NMR peaks still could not be separated.

To resolve the two different Al sites spectroscopically, ^{27}Al MAS NMR experiments at multiple magnetic fields, satellite transition NMR, and multiple-quantum MAS techniques have been utilized. Although these NMR experiments failed to resolve the two Al sites, the spectra have been interpreted with the aid of theoretical ab initio quantum mechanical modeling using full potential linearized augmented plane wave (FP-LAPW) model and the CASTEP software program. Average values of C_q, η, and δ_{iso} for the two Al sites were constrained to be 2.6 MHz, 0.75 and 6.25 ppm with high confidence.

Keywords: Kaolinite, ^{27}Al MAS NMR, multiple-quantum MAS, satellite transition NMR, multiple magnetic fields, FP-LAPW modeling, CASTEP, quadrupolar interaction parameters