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The two aluminum sites in the ^{27}Al MAS NMR spectrum of kaolinite: Accurate determination of isotropic chemical shifts and quadrupolar interaction parameters

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Abstract

The problem of resolving the two aluminum sites in the ^{27}Al NMR spectrum of kaolinite has been unsuccessfully addressed for 30 years. A few years ago, it was shown that the two sites cannot be spectrally separated even by the use of high magnetic fields. Nevertheless, it is still possible to determine the NMR parameters of both sites. In this article, we present an alternative approach. We show that, at low magnetic field (7 T), the individual spinning sideband lineshapes of the outer satellite transitions are sensitive enough to differentiate information coming from the two aluminum sites. Thus, the isotropic chemical shift δ, the quadrupolar constant C_Q, and asymmetry parameter η_Q of each site can be obtained by accurately fitting the full ^{27}Al MAS spectrum acquired at low magnetic field. In return, this approach requires a carefully acquired and post-treated ^{27}Al spectrum. It is concluded that the two sets of parameters (δ = 7.5 ppm, C_Q = 3.4 MHz, η_Q = 0.8) and (δ = 8.0 ppm, C_Q = 3.0 MHz, η_Q = 0.9) represent the best and the unique solution overall. Moreover, the accuracy of these experimental values is independently and fully supported by first-principles calculations of the electric field gradient.

The approach presented in this article can be easily applied, not only to clays or aluminosilicate materials, but to any compounds where the NMR parameters of overlapping spectral lines have to be determined. This can also be extended to sites of unequal multiplicity and to other nuclei. Moreover, this methodology can be useful in the characterization of small structural changes occurring partly at one particular site. Indeed, when the NMR parameters are barely modified, the spectral signatures due to both affected and unaffected sites may strongly overlap, making the spectral resonances broad and badly resolved. In such a case, determining the isotropic chemical shift and the quadrupolar coupling parameters may help to exceed the simple qualitative analysis of structural changes by offering the possibility of discriminating between structural models via the experimental data.

Keywords: Kaolinite, ^{27}Al MAS NMR, isotropic chemical shift, quadrupolar parameters, EFG calculations