

Multiple oxygen sites in synthetic phyllosilicates with expandable layers: ¹⁷O solid-state NMR study

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ABSTRACT

Recent advances in high-resolution solid-state NMR enabled us to resolve the previously unknown details of atomic configurations around quadrupolar nuclides such as O (¹⁷O, spin 5/2) and aluminum (²⁷Al, spin 5/2) in phyllosilicates. Here, we report the ¹⁷O 1D and 2D NMR (MAS and MQMAS) spectra of synthetic kaolinite-montmorillonite mixtures. Various O sites in the mixtures revealed from O-17 NMR include apical O (^{VI}Si-O-2^{IV}Al), multiple basal O atoms (^{VI}Si-O-^{VI}Si and two ^{VI}Si-O-^{VI}Al sites) in tetrahedral layers, and hydroxyl group with distinct ranges for NMR parameters (quadrupolar coupling constant, C_q and isotropic chemical shift, ¹⁷O δ_{iso}). In particular, the structurally relevant NMR parameters (¹⁷O δ_{iso}, C_q, and asymmetry parameter, η) for two resolved ^{IV}Si-O-^{VI}Al sites are about 52 ± 2 ppm, 2.6 ± 0.2 MHz, and 0.5 for ^{IV}Si-O-^{IV}Al (I) and about 44.5 ± 2 ppm, and 3.1 ± 0.2 MHz, and 0.5 for ^{IV}Si-O-^{IV}Al (II), respectively. These sites may stem from crystallographically distinct ^{IV}Si-O-^{IV}Al sites of varying bond length and ^{IV}Si-O-^{VI}Al bond angle or ^{IV}Al-O-2^{VI}Al site in the montmorillonite.

Keywords: High-resolution solid-state NMR, phyllosilicates, oxygen sites, 3QMAS NMR, montmorillonite