American Mineralogist, Volume 92, pages 397–402, 2007

Organic anions in layered double hydroxides: An experimental investigation of citrate hydrotalcite

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ABSTRACT

The nature of the chemical interactions between organic species and mineral surfaces and interlayers has significant implications for many geochemical processes and for medical and materials applications, but the molecular-scale characteristics of such interactions are poorly understood. Here we describe an experimental investigation of citrate-hydrotalcite (HT) that is designed to investigate the structural environments and dynamical behavior of carboxylic species interacting with the protonated surfaces of positively charged materials such as layered double hydroxides (LDHs). X-ray diffraction, compositional analysis, and thermal analysis confirm successful intercalation of trivalent citrate anions into the interlayers of the Mg/Al hydrotalcite using an ion-exchange method. The basal spacing changes from 8.9 Å at relative humidity (R.H.) = 0% to 11.3 Å at R.H. = 75%, to 18.9 Å at 100% R.H., consistent with reorientation of the citrate from parallel to the hydroxide layers at low water contents to perpendicular to them at higher water contents. At the largest water contents, the citrate may lose contact with one of the hydroxide layers, in contrast to the behavior of LDHs containing small, inorganic species. The similarity of the ^{13}C nuclear magnetic resonance (NMR) chemical shifts for citrate-HT and sodium citrate solution demonstrates the absence of grafting (covalent bond formation) between the citrate molecules and the metal hydroxide layers, and the dominance of Coulombic and H-bond interactions in stabilizing the structure. Decreasing ^{13}C NMR peak widths, decreasing signal/noise ratios in the ^{1}H-^{13}C CPMAS NMR spectra, and increasing basal spacing with increasing R.H. are consistent with increasing dynamical disorder of the interlayer citrate sites in a progressively more water-rich interlayer.

Keywords: Citrate- HT, ion-exchange, XRD, thermal analysis, ^{1}H-^{13}C CPMAS NMR