^{113}Cd CP-MAS NMR spectra of cadmium hydroxides containing various anions in their structures

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Behavior of cadmium ion (Cd^{2+}) in environment is greatly concerned because of its strong toxicity. In soil sphere, Cd^{2+} has been thought to adsorb onto surface of soil particles by forming inner sphere complexes. With increasing the surface coverage of Cd^{2+}, they may convert to hydroxide (β-$Cd(OH)_2$). However, hydrolysis of cadmium salts aqueous solutions at pH and ionic strength found in natural environment revealed that hydrolysis products obtained were not β-$Cd(OH)_2$ but double salts containing co-existing anions in their structure. In this study, hydrolysis product of Cd^{2+} containing various anion species, especially NO_3^-, were measured by ^{113}Cd CP-MAS NMR, and attempt was made to assign each peak comparing to XRD results.

Hydrolysis of cadmium ion was performed by adding sodium hydroxide aqueous solution to cadmium nitrate, sulfate, and chloride. Solid samples were collected in the course of hydrolysis. The ^{113}Cd CP-MAS NMR spectra were recorded on JEOL ECA 400 spectrometer operating at 88.7 MHz. The chemical shift was relative to 1.0 M $Cd(ClO_4)_2$. The spinning rate of the sample tube for solid samples was 13 kHz. Acquisition time and the pulse delay were changed depending on the samples.

XRD patterns revealed that we succeeded in obtaining almost pure nitrate double salts, $Cd_5(OH)_8(NO_3)_2{\cdot}2H_2O$ and $Cd(OH)NO_3{\cdot}H_2O$. ^{113}Cd CP-MAS NMR spectrum of $Cd(OH)NO_3{\cdot}H_2O$ had a simgle peak at -9 ppm, while $Cd_5(OH)_8(NO_3)_2{\cdot}2H_2O$ showed two peaks at around 140 and 100 ppm. Interestingly, the peak at around 140 ppm observed for $Cd_5(OH)_8(NO_3)_2{\cdot}2H_2O$ splitted in 3 peaks, while β-$Cd(OH)_2$ showed a single peak at 140 ppm. A sample, in which XRD pattern suggested coesitence of $Cd_3(OH)_5NO_3$ showed peaks at 95 and 159 ppm. All these peaks found in ^{113}Cd CP-MAS NMR spectra were assigned to specific coordination environment around Cd by comparing crystallographic structures of double salts.