

²⁷Al Solid-state NMR Structural Studies of Hydrotalcite Compounds Calcined at Different Temperatures

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Hydrotalcites are anionic clays that are quite prevalent in nature and their importance is growing more and more because of their very wide range of potential applications and uses. Understanding the structural and compositional changes that occur on the molecular scale during the thermal decomposition of hydrotalcite compounds is essential for the basic prediction and comprehensive understanding of the behavior and technical application of these materials. In this study, several hydrotalcite compounds calcined at different temperatures for applications in a chlorine resistant textile were prepared and ²⁷-Aluminum solid-state nuclear magnetic resonance (NMR) spectroscopy was used as a tool to study their local structure and behavior. The changes in the Al coordination of the hydrotalcite compounds were investigated with one dimensional (1D) solid-state magic angle spinning (MAS) NMR spectroscopy. The two broad resonances arising from the structurally different Al coordinations of these compounds were clearly resolved by two dimensional (2D) triple quantum magic angle spinning (3QMAS) NMR spectroscopy.

Key Words: Hydrotalcite, Solid-state NMR, ²⁷Al NMR, 1D MAS, 2D 3QMAS

Introduction

Hydrotalcites are one of a few species of minerals with significant, permanent anion-exchange capacity, which stand in contrast to the more common clay minerals having cation-exchange properties, and are quite prevalent in nature.¹ Ideal hydrotalcites have a structural formula of Mg₆Al₂(OH)₁₆CO₃·4H₂O and consist of positively charged brucite-type octahedral sheets.² Anions and water molecules are incorporated in the interlayer spacing, with carbonate ions being especially rigidly held.³⁻⁷ The net positive charge on the octahedral sheets is due to the partial substitution of Al for Mg.⁷

The recent interest in the study of hydrotalcites results from their extensive range of potential applications. For example, hydrotalcites may be used as a component in nano-materials such as nano-composites.⁸ They are also important in the removal of environmental hazards in acid mine drainage.^{9,10} Coincidentally, their formation offers a mechanism for the management of hazardous chemical and radioactive waste or a means of heavy metal removal from contaminated waters.^{11,12} Of particular importance is their use in wastewater treatment, specifically for the removal of anions such as arsenate or cyanide.¹³ The basis of these potential applications is the ability to make mixed metal oxides at the atomic level, rather than at the particle level. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite.^{14,15} In most cases, hydrotalcite compounds calcined at high temperatures were used for the removal of arsenate, chromate, vanadate and chloride ions from water solution. In this study, several hydrotalcite compounds calcined at different temperatures were prepared, and were then applied in a chlorine resistant textile that was specially engineered to allow swimwear and underwear to last longer after exposure to chlorine in swimming pools or washing in bleach and to maintain its elasticity and color consistency.

Understanding the structural and compositional changes

that occur on the molecular scale during the thermal decomposition of hydrotalcite compounds is essential for the basic prediction and comprehensive understanding of the behavior and technical application of these materials. However, the structural environments and dynamical behavior of the interlayer and surface species of hydrotalcites are difficult to study and poorly understood. In this study, ²⁷Al solid-state nuclear magnetic resonance (NMR) spectroscopy was used as a tool to study their local structure and behavior.¹⁶⁻¹⁹ We recently investigated the structural changes of several hydrotalcite compounds calcined at different temperatures in the range from 433K to 513K by 1D MAS solid-state NMR spectroscopy.²⁰ In this study, we obtained 1D MAS spectra with 18 kHz magic-angle sample spinning with improved resolution and sensitivity compared to the previous data. When nuclei have a spin value of I = 1/2, the MAS technique allows for the easy high-resolution analysis of all of the different species. However, most Al resonances are quite broad because ²⁷Al nuclei have a nuclear spin of 5/2 and are subjected to a quadrupole interaction resulting from the coupling between their quadrupole moment and the electric field gradients. This interaction is very sensitive to the local atomic surroundings and can be used as an effective microscopic probe.²¹ For example, it has often been used in single crystals to analyze the changes resulting from second-order or even incommensurate phase transitions.²² For this reason, it has been proposed as an elegant 2D multiple quantum magic angle spinning (MQMAS) method allowing for the easy correlation between the high resolution (isotropic) spectrum along ν₁ and the MAS spectrum along ν₂.²³⁻²⁵ In this paper, we present the first clear characterization of the two broad resonances arising from the different Al coordinations of hydrotalcite by ²⁷Al 2D z-filtered 3QMAS NMR spectroscopy.^{21,23} This technique may also provide a means of characterizing complex and heterogeneous natural layer structures and other nanoscale materials, such as crystalline and amorphous compounds.

Experiments

The hydrotalcite compounds before and after calcinations and standing for 24 hours after calcinations at room temperature and humidity, which are referred to as HT_B, HT_A, and HT_O respectively were prepared as described in our previous study.²⁰ And various hydrotalcite compounds calcined at different temperatures of 433K, 453K, 473K, 493K, and 513K, which are referred to as HT₄₃₃, HT₄₅₃, HT₄₇₃, HT₄₉₃, and HT₅₁₃ respectively were prepared. A textile treated with HT_A, which is referred to as HT_T were prepared also. All hydrotalcite compounds were prepared as described in our previous study.²⁰

The ²⁷Al solid-state MAS NMR spectra used for determining the Al conformations of the hydrotalcite compounds were collected using a unityINNOVA wide bore NMR spectrometer (Varian, US) with a magnetic field of 9.4 Tesla operating at a ²⁷Al Larmor frequency of 104.21 MHz. A 4-mm triple resonance CPMAS probe (T3 probe Varian, US) was used to obtain the spectra with a spinning rate of 17 to 18 kHz. The magic angle was set using the ⁷⁹Br resonance of KBr. The ²⁷Al chemical shifts were referenced to the center of the octahedral resonance of Al₂O₃ at 0 ppm. The hydrotalcite compounds were ground with a mortar and pestle, and then were packed in a 4 mm zirconia rotor with a vespel drive tip, PTFE spacer, and end cap. All of the measurements were taken at ambient temperature of 20 to 24°C.

In the 1D single pulse MAS experiments, the spectra of the hydrotalcite compounds calcined at different temperatures were collected with a spinning rate of 18 kHz, and the other spectra were collected at 17 kHz. The number of scans was 1024 using a relaxation delay of 1 sec, and the $\pi/2$ excitation pulse width was 2.2 μ sec for all of the 1D MAS experiments. The spectral width was set to 1 MHz to eliminate the folding of the resonances caused by the typically non-negligible second order anisotropic distributions of the chemical shifts of 800 kHz.

In the 2D z-filtered 3QMAS experiment, the spectra of the hydrotalcite compounds calcined at different temperatures were collected with a spinning rate of 17 kHz, and a relaxation delay of 0.2sec was used through the optimization. The ²⁷Al 3QMAS spectra were obtained using a pulse sequence consisting of two hard non-selective pulses and one optional lower-power selective $\pi/2$ pulse.^{21,27} This sequence uses the z filtered, hypercomplex phase cycle of Amoureux *et al.*, which is incremented in 90 degree steps and requires a minimum of 24 steps.^{21,27} Optimized first pulse duration was 6.3 μ sec and the second MQ conversion pulse duration was 2.1 μ sec in CW conversion mode. The final z-filter pulse duration was 10 μ sec. The z-filter delay time between the second pulse and the third pulse was 10 μ sec. t1 increments of 64 were used for a spectral width of 50 kHz and phase mode was selected the cosine and sine hypercomplex datasets for pure-phase 2D spectra. The tetrahedral site of the hydrotalcite compounds has very low intensity, therefore, 1200 scans per increment were used with 1024 complex data points to get a sufficient signal-to-noise ratio and it took about 10 hours to acquire each spectrum.

The processing and comparison of the 1D MAS spectra were carried out using Topspin 1.3 (Bruker, Germany), and the

2D 3QMAS spectra were processed and analyzed by VNMRJ 2.1B (Varian, US). In the ²⁷Al 1D MAS spectra, the FIDs were zero-filled to 32k points. In the 2D 3QMAS spectra, both dimensions were zero-filled to 2048 points and a dataset was processed as a pure-phase spectrum based on two datasets with sine and cosine phases. The data was shear transformed, which was accomplished by incrementing the first order phase for each spectrum, in the indirect dimension according to the procedure of Massiot *et al.*^{26,27}

Results and Discussion

The ²⁷Al 1D MAS NMR spectra of samples HT_B, HT_A and HT_O are shown in Figure 1. The ²⁷Al MAS spectrum of the HT_B sample before calcination shows a relatively narrow resonance peak at a chemical shift, δ , of \sim 1.6 ppm, which represents the octahedral coordination (0–10 ppm) of Al.²⁸ On the other hand, the spectra of sample HT_A after calcination at high temperature and sample HT_O which was left for 24 hours after calcination show a broader Al resonance of the octahedral coordination compared to that of HT_B. In addition, their spectra show a broad and small resonance at \sim 64 ppm, which represents the tetrahedral coordination (40–80 ppm) of Al, and there is little difference between the spectra of HT_A and HT_O.²⁸

The ²⁷Al MAS NMR spectra of the hydrotalcite compounds calcined at various temperatures are compared in Figure 2. As the calcination temperature increased, the intensity of the Al resonance at the tetrahedral site was gradually increased. The intensity of the Al resonance at the octahedral site, however, became smaller and broader. The ²⁷Al NMR signal arising from the amorphous Al₂O₃ phase near about 20 ppm, which represents the right edge of the octahedral coordination, is the octahedral coordination, is the main factor contributing to the

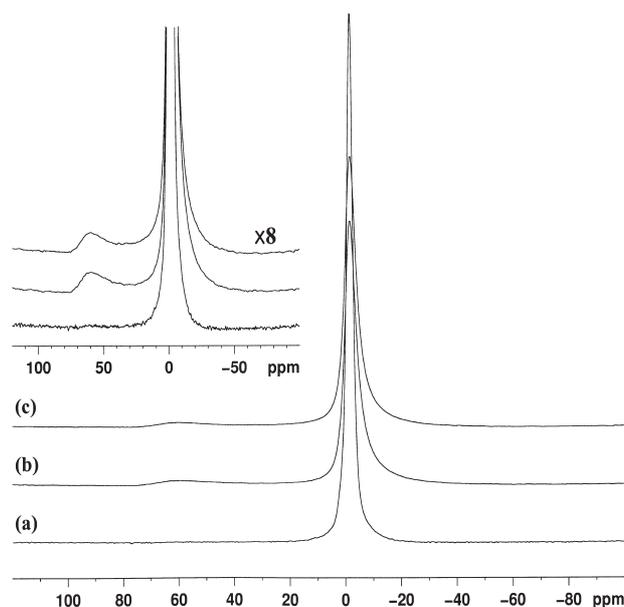


Figure 1. ²⁷Al 1D MAS solid-state NMR spectra of HT_B(a), HT_A(b) and HT_O(c). HT_B is before calcination, HT_A is after calcination at high temperature, and HT_O is after calcination and being left to stand for 24 hrs at room temperature and humidity.

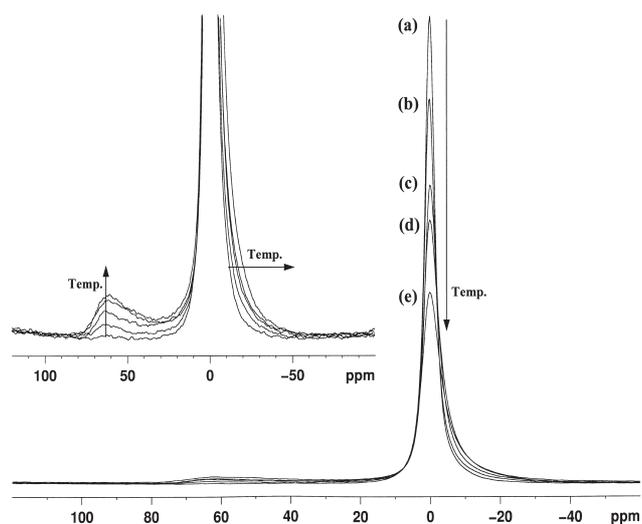


Figure 2. ^{27}Al 1D MAS solid-state NMR Spectra of the hydrotalcite compounds, (a) HT₄₃₃ (b) HT₄₅₃ (c) HT₄₇₃ (d) HT₄₉₃ (e) HT₅₁₃, calcined at various temperatures. As the calcination temperature rises, the spectra were shifted in the directions of the arrows.

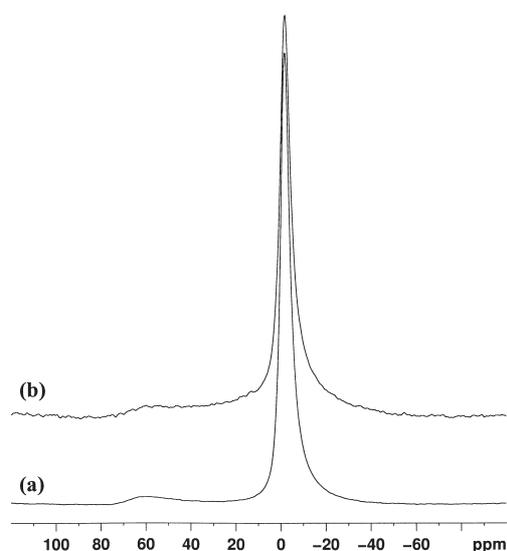


Figure 3. The ^{27}Al 1D MAS solid-state NMR spectra of HT_A(a) and HT_T(b) are shown. HT_A is after calcination at high temperature and HT_T is the textile treated with less than 5% of sample HT_A.

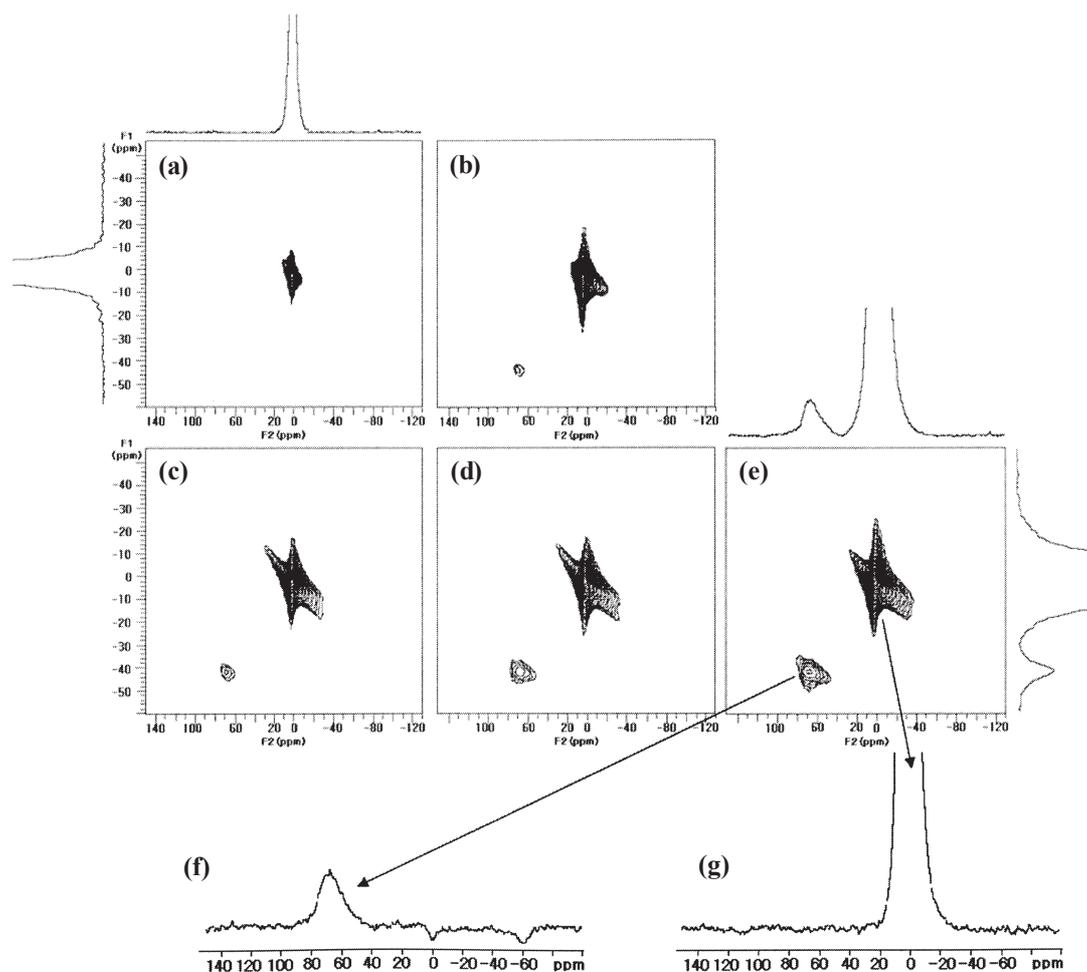


Figure 4. ^{27}Al 2D z-filtered 3QMAS solid-state NMR spectra of the hydrotalcite compounds, (a) HT₄₃₃, (b) HT₄₅₃, (c) HT₄₇₃, (d) HT₄₉₃, and (e) HT₅₁₃, calcined at various temperatures. All of the spectra were acquired with a spinning speed of 17 kHz. The sheared ^{27}Al 3QMAS spectrum is a two-dimensional Fourier transform plot of a triple/single-quantum correlation to highlight the isotropic and anisotropic nature of the ^{27}Al in these compounds. In this contour plot, the v2 dimension represents single quantum coherence or isotropic and anisotropic coherence. The f1 dimension represents the multiple quantum dimension and only contains information about isotropic coherences. The anisotropic projections resolved from the 2D 3QMAS spectra of (e) are presented parallel to the horizontal axis under the 2D spectra; (f) is an anisotropic projection of the tetrahedral site, while (g) is an anisotropic projection of the octahedral site.

line broadening and asymmetrical shape of the octahedral resonance.

HT_T, which is the textile treated HT_A sample, was also investigated by ²⁷Al MAS solid-state NMR spectroscopy. A comparison of the spectra between HT_T and HT_A is shown in Figure 3.

The spectrum of HT_T is very similar to that of HT_A, although an observable spectrum with a sufficiently low signal-to-noise ratio was achieved at the expense of a long acquisition time requiring a large number of scans, 8192, because of the very low content (less than 5%) of Al in the textile.

We performed a ²⁷Al 2D z-filtered 3QMAS experiment on the hydrotalcite compounds calcined at various temperatures (HT₄₃₃-HT₅₁₃) to obtain clearer the ²⁷Al resonances. The sheared ²⁷Al 3QMAS spectra are shown in Figure 4 with the horizontal axis representing the MAS spectrum dimension and the vertical axis representing the high resolution isotropic spectrum dimension. Two isotropic resonances on the v1 dimension were observed with an anisotropic projection on the v2 dimension in the spectra shown in Figure 4 (a) and (e).

The projection data are consistent with the ²⁷Al 1D MAS NMR results. From the ²⁷Al 2D z-filtered 3QMAS spectra, we also found that, as the calcination temperature rises, the contour corresponding to the tetrahedral site becomes bigger, and the contour corresponding to the octahedral site becomes broader. The 2D lineshapes were observed to smear as expected, especially near the octahedral site region. The fact that there is smearing in the ²⁷Al 3QMAS data indicates the existence of amorphous Al₂O₃ phase, as suggested by the ²⁷Al 1D MAS NMR results. The anisotropic projections, resolved from the 2D 3QMAS spectra of the HT₅₁₃ sample shown in Figure 4(e), are presented in Figure 4(f) and (g) parallel with the horizontal axis. The MAS spectra in Figure 4(f) and (g) are distorted compared to those obtained from the single-pulse MAS experiments because of the non-uniform excitation conditions.

Conclusions

The changes in the Al coordination of hydrotalcite compounds during heat treatment were investigated by ²⁷Al 1D MAS and ²⁷Al 2D z-filtered 3QMAS solid-state NMR spectroscopy. The conformation of Al is changed from octahedral coordination to tetrahedral coordination after calcinations above 453 K, indicating that it strongly depends on the calcination temperature.

The adsorbed and interstitial water is removed from the interlayer at temperatures above approximately 453 K. At higher temperatures (above 453 K), the hydrotalcite undergoes dehydroxylation and decarboxylation. Therefore, tetrahedral coordinated Al centers are created and an amorphous Al₂O₃ phase is formed. The textile treated with hydrotalcite also shows two kinds of Al coordination, even though the content of Al is less than about 5%. The two anisotropic resonances arising from the structurally different Al coordinations of the hydrotalcite

were clearly resolved by ²⁷Al 2D z-filtered 3QMAS NMR spectroscopy. This technique may also be used to resolve the resonances in inorganic compounds or for the study of nanocrystals containing quadrupole nuclei.

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