



Structural Studies of Hydrotalcite Compounds Calcined with Different Temperatures by ^{27}Al Solid-state NMR Spectroscopy

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Abstract : Several hydrotalcite compounds calcined with different temperature for applications in a chlorine resistant textile were prepared, and its structural changes in dependence on the temperature were studied by using ^{27}Al solid-state nuclear magnetic resonance(NMR) spectroscopy. We found that the Al coordination was partly lowered from octahedral to tetrahedral site as the calcined temperature goes up. And we also investigated the hydrotalcite-treated textile for chlorine resistance by using ^{27}Al solid-state NMR spectroscopy.

Keywords: NMR, solid-state NMR spectroscopy, structure, hydrotalcite, Aluminum

INTRODUCTION

Hydrotalcite is one of a few minerals with significant, permanent anion-exchange capacity, and stands in contrast to the more common clay minerals which have cation-exchange properties. Ideal hydrotalcite has a structural formula of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ and consists of positively charged brucite-type octahedral sheets, alternating with interlayers containing carbonate anions and water molecules.¹⁻⁶ The net positive charge on the octahedral sheets is due to the partial substitution of Al for Mg. Hydrotalcite compounds calcined at high temperature were used for the removal of arsenate, chromate, vanadate ion, and chloride ion from water solution.⁷⁻⁸ They also have potential applications in a chlorine resistant textile which has been specially engineered to allow swimwear and underwear to

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last longer after exposure to chlorine in swimming pools or washing in bleach and to maintain its elasticity and color consistency.^{9,10} In this study, structural changes of several hydrotalcite compounds calcined with different temperature from 433K to 513K were studied. Changes in the Al coordination of the hydrotalcite compounds were investigated with ²⁷Al Solid-state NMR spectroscopy.

EXPERIMENTAL

Sample preparation

Three kinds of hydrotalcite compounds, HT₀ which is before calcination, HT_A after calcination at high temperature and HT_B which was left for 24 hours at room temperature and room humidity after calcinations were supplied from Hyo-Sung Corporation. Additionally, the various hydrotalcite compounds calcined with different temperature at 160, 170, 180, 190, 200, 220, 240 °C, and textile treated HT_A, which is called HT_T, were also provided by Hyo-Sung.

Characterization

Aluminum conformations of hydrotalcite compounds was determined by ²⁷Al aluminum solid-state nuclear magnetic resonance spectroscopy using 9.4Tesla *unityINOVA* wide bore NMR spectrometer (Varian, US) operating at a ²⁷Al NMR frequency of 104.21 MHz and a ¹H NMR frequency of 399.92MHz using Al₂O₃ as a external chemical shift standard at 0 ppm. Hydrotalcite compounds were ground with a mortar and pestle, and then were packed in a 4mm ZrO₂ rotor. A Triple-resonance 4mm CPMAS probe, which is called T3 probe, (Varian, US) was used. All of the measurements were taken at room temperature. One pulse experiment on hydrotalcite compounds calcined with different temperature was carried out at Magic Angle Spinning (MAS) frequencies of 15 KHz spinning speed.^{11,12} The magic angle was set using the ⁷⁹Br resonance of KBr. ²⁷Al magnetization was generated at a field of 62.5 KHz and spectral width was set to 1 MHz. The number of scans was 512 using a recycle delay of 1 s. Analysis and comparison of spectra were carried out using WINNMR (Bruker, Germany).

RESULTS AND DISCUSSION

^{27}Al NMR Spectra of HT_0 , HT_A and HT_B were showed in Fig. 1. The NMR spectrum of HT_0 shows a relatively narrow resonance peak at chemical shift δ of ~ 1.6 ppm corresponding to octahedral coordination of Al conformation. On the other hand, a broad resonance related to tetrahedral coordination of Al was found in ~ 64 ppm for HT_A . And there was little difference between HT_A and HT_B spectra.

^{27}Al NMR Spectra of the hydrotalcite compounds calcined with various temperatures were compared in Fig. 2. As the calcined temperature rises, the tetrahedral coordination of Al is gradually increased and the octahedral Al resonance was getting broader. Therefore, less coordinated Al centers are created and an amorphous Al_2O_3 phase near -20 ppm is formed.

HT_T , which is a textile treated with HT_A , was also investigated with ^{27}Al solid-state NMR spectroscopy. The spectrum of HT_T was similar to the spectrum of HT_A although the number of scans of 8192 is much more than 512 of HT_A , because of very small contents of Al in a textile.

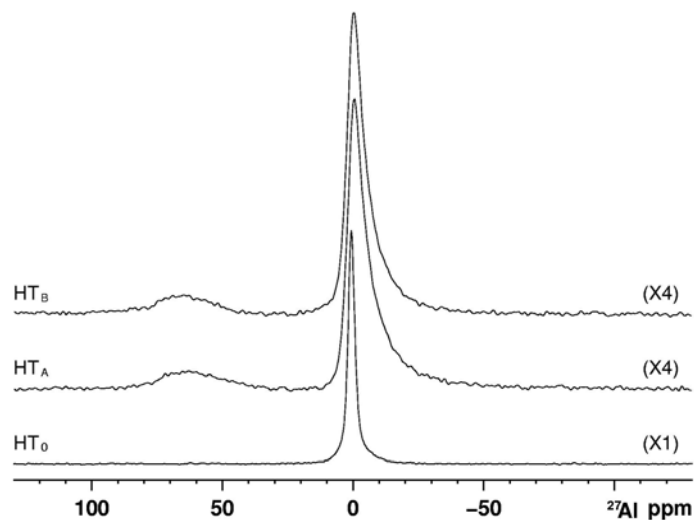


Fig. 1. ^{27}Al Solid-state NMR spectra of HT_0 , HT_A and HT_B are showed. HT is before calcination, HT_A is after calcination at high temperature, and HT_B is left for 24 hrs at room temperature and room humidity after calcinations.

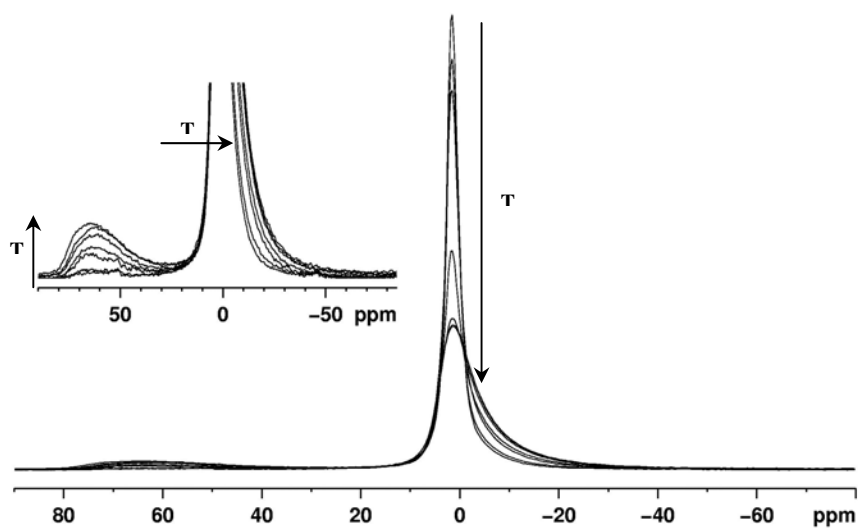


Fig. 2. ^{27}Al Solid-state NMR Spectra of the hydrotalcite compounds calcined with various temperatures. Arrow means the changes according to direction of increasing temperature from 433 K to 493 K.

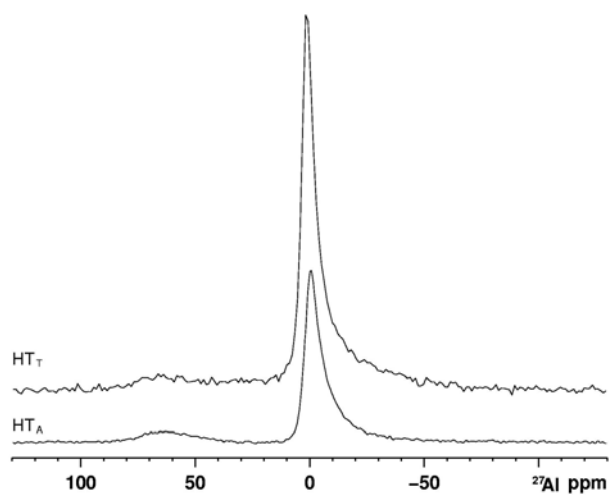


Fig. 3. ^{27}Al Solid-state NMR spectra of HT_A and HT_T are showed. HT_A is after calcination at high temperature. And HT_T is a textile treated with very small amounts of hydrotalcite HT_A .

CONCLUSIONS

The changes in the coordination at the Al sites during heat treatment are investigated by ^{27}Al Solid-state NMR study. The coordination of Al is changed from octahedral to tetrahedral after calcination above 453 K based on the Fig. 2. It strongly depends on the function of the calcinations temperature. Adsorbed and interstitial water is removed from the inter-layer at temperatures above approximately 443 K. At higher temperatures (>453 K), the hydrotalcite might undergo dehydroxylation and decarboxylation. Therefore, less coordinated Al centers are created and an amorphous Al_2O_3 phase is formed. Based on the Fig. 3, a textile treated with hydrotalcite also shows Al coordination even though the content of Al is a lot less than about 5%.

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REFERENCES

1. Reichle, W.T., *Solid State Ionics*, **22**, 135 (1986).
2. Bellotto M. et al., *Journal of Physical Chemistry*, **100**, 8527 (1996).
3. Hansen, H.C.B., R.M., *Clay Minerals*, **26**, 311 (1991).
4. Dupuis J. et al., *Solid State Ionics*, **42**, 251 (1990).
5. Marcelin G. et al., *Journal of Physical Chemistry*, **93**, 4646 (1989).
6. van der Pol A. et al., *Journal of Physical Chemistry*, **98**, 4050 (1994).
7. Cavani F., Trifiro F., Vaccari A., *Catalysis Today*, **11**, 173 (1991).
8. Moini A., Pinnavaia T. J., *Solid State Ionics*, **26**, 119 (1988).
9. E. R. Andrew, A. Bradbury, R. G. Eades, *Nature*, **182**, 1659 (1958).
10. I. J. Lowe, *Phys. Rev. Lett.* , **2**, 285 (1959).
11. A. Samoson, E. Kundla , E. Lippmaa, *J. Magn. Reson.*, **49**, 350 (1982).

12. S. Schramm, E. Oldfield, *J. Am. Chem. Soc.*, **106**, 2502 (1984).