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Coordination Structure of Aluminum in Magnesium Aluminum Hydroxide Studied by ^{27}Al NMR

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Abstract: The coordination structure of aluminum in magnesium aluminum hydroxide was studied by ^{27}Al NMR. The result showed that tetrahedral aluminum (Al^{IV}) existed in magnesium aluminum hydroxide, and the contents of Al^{IV} increased with the increase of the ratio of Al/Mg and with the peptizing temperature. Al^{IV} originated from the so-called Al_{13} polymer with the structure of one Al tetrahedron surrounded by twelve Al octahedrons.

Keywords: Coordination structure, magnesium aluminum hydroxide, ^{27}Al NMR.

Magnesium aluminum hydroxide belongs to anionic clay, and it was known as layered double hydroxides (LDHs). The crystal structure[1,2,3] of magnesium aluminum hydroxide is hydrotalcite-like which belongs to the hexagonal system. In each monolayer, Mg^{2+} and Al^{3+} are randomly distributed within the same octahedral hydroxide sheet, the positive charge on the hydroxide sheets is balanced by interlayer exchangeable anions such as Cl^- and OH^-.

In the past decade, the charge mechanism of magnesium aluminum hydroxide was thought of as the replacement of some of Mg^{2+} by Al^{3+} isomorphously, resulting a net positive charge on the hydroxide sheets[4]. However, this mechanism has not been proved by experiment. The aim of this paper is to study the coordination structure of aluminum in magnesium aluminum hydroxide by ^{27}Al NMR technique, and to make further discussion on the charge mechanism of magnesium aluminum hydroxide.

Experimental

$AlCl_3{\cdot}6H_2O$; $MgCl_2{\cdot}6H_2O$; $NH_3{\cdot}H_2O$ were in C.P. grade. ^{27}Al solid-state spectra were recorded at room temperature on American Varian UNITY plus-400 model spectrometer with solid cp/MAS probe. Its resonance frequency was 104.243 MHz, with the pulse width of 0.5μs and recycle delay of 0.5 s. The rotating speed of the motor was 8 KHz, and the reference of chemical shifts was $Al(NO_3)_3$.

^{27}Al aqueous solution spectra were recorded at room temperature on JEOL FX-90Q

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NMR spectrometer. Its resonance frequency was 23.34868 MHz, with the pulse width of 40 ms, cumulative times of 1000, and spectral width of 5000 Hz, respectively.

Prior to measurements the solid aluminum hydroxide, prepared according to the literatures[1,2], the sample was first transformed into powder by heating at 105°C±0.5 for 4 h.

Results and Discussion

Solid state ^{27}Al MAS NMR spectrum of $Al(OH)_3$ is shown in **Figure 1 (a)**. A strong peak at 0 ppm due to octahedral aluminum (Al^{VI}) (the Roman numbers VI and IV stand for the coordination number of aluminum with respective oxygen), two weak but clearly visible peaks at ±80 ppm, and a shoulder at 100 ppm due to aluminum-rotation were observed as shown in **Figure 1 (a)**. This result showed that in aluminum hydroxide only Al^{VI} existed without any other coordination structure of aluminum.

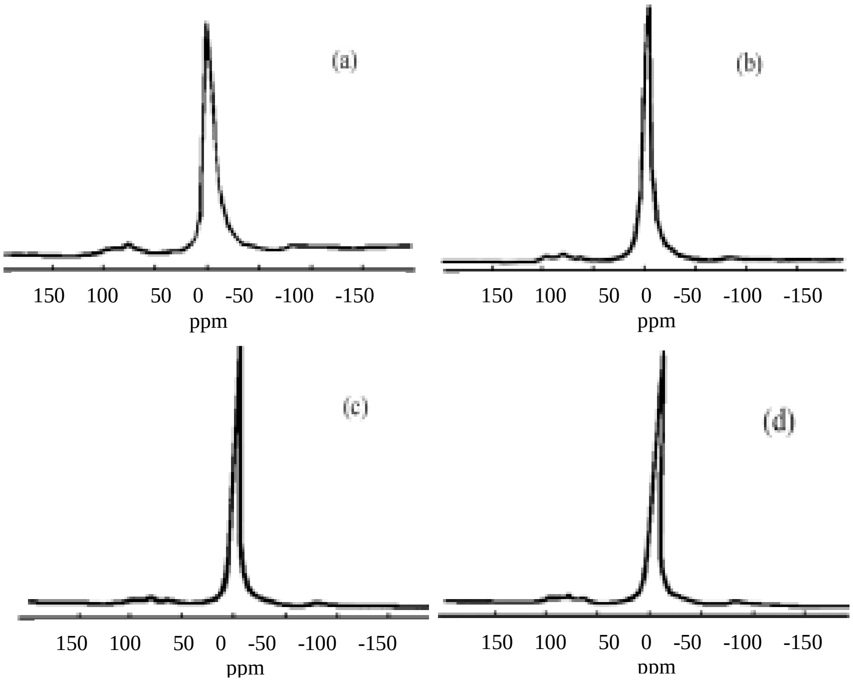
Figures 1 (b), (c), (d) are the spectra of magnesium aluminum hydroxide. Besides above mentioned four peaks, a new shoulder at 65 ppm appeared. At the same time, the chemical shift of Al^{VI} shifted from 0 ppm to 1.69 ppm. We thought that the new shoulder at 65 ppm was caused by tetrahedral aluminum (Al^{IV}). Plee *et al.*[5] reported that the peak at 59 – 63 ppm was most probably due to the Al^{IV} in the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ polymer, and the peak at 67 – 69 ppm was due to the Al^{IV} in the clay itself. On the other hand, the contents of Al^{IV} increased from 0.5% to 2.5% with the increase of the ratio of Al/Mg from 1: 0.9 to 1:1.9, and Al^{IV} increased from 2.5% to 3.3% with the increase of the peptizing temperature (from 80°C to 200°C) (see **Figure 1**). The higher the peptizing temperature, the easier the structure transformed from Al^{VI} to Al^{IV}.

The reason of existence of Al^{IV} in magnesium aluminum hydroxide is that an intermediate of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (denoted as Al_{13}) was formed during preparation, which possessed the structure of one Al tetrahedron surrounded by twelve Al octahedrons. The NMR spectrum of this species (in aqueous solution only) had a peak at 63 ppm (see **Figure 2**), which was assigned to Al^{IV} in Al_{13} polymer by Bottero *et al* [6]. The Al_{13} concentration depended on OH/Al ratio (r value). The r value increased from o to 2.2 the concentration of Al_{13} increased; but when r value increased further from 2.2 to 2.5, the concentration of Al_{13} decreased.

The above mentioned results could be successfully used to explain that Al^{IV} did not exist in $Al(OH)_3$ but existed in magnesium aluminum hydroxide. As known $Al(OH)_3$ was prepared at r>3.0. However, Al^{IV} did not exist in aqueous solution, if r>2.5(see **Figure 2**). Therefore, Al^{IV} did not exist in $Al(OH)_3$. During the formation of magnesium aluminum hydroxide, Mg^{2+} intercalated into the crystal lattice of $Al(OH)_3$ making $Al(OH)_3$ bear positive charge. In order to balance the positive charge and maintain the stability of structure, Al^{IV} was preserved in magnesium aluminum hydroxide.

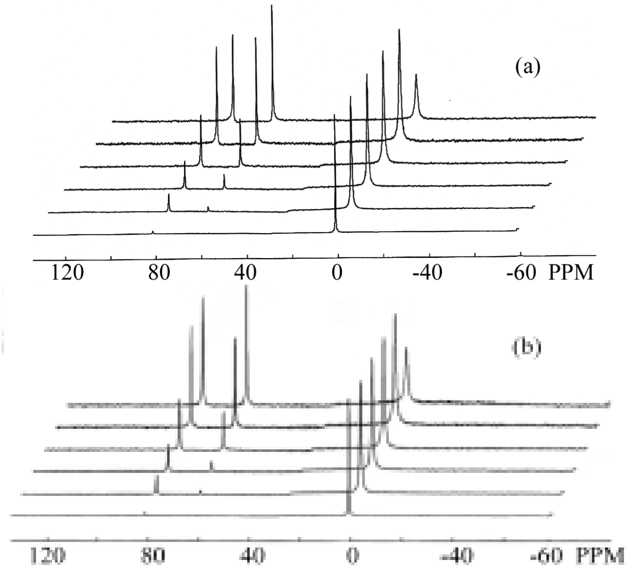
From the above analysis, a conclusion may be drawn that magnesium ions intercalated the crystal lattice of $Al(OH)_3$, making in magnesium aluminum hydroxide bore positive charge rather than some of Mg^{2+} were replaced by Al^{3+} in the crystal lattice.

Figure 1 Solid state ^{27}Al MAS NMR spectra of magnesium aluminum hydroxide



(a). Al(OH)$_3$ (b). Al:Mg=1:0.9; Peptizing temperature at 80°C. (c). Al:Mg=1:1.9; Peptizing temperature at 80°C. (d). Al:Mg=1:1.9; Peptizing temperature at 200°C.

Figure 2 ^{27}Al NMR spectra in aqueous solution at varied r value



(a). From top to down r value was 2.5, 2.3, 2.0, 1.5, 1.0, 0, respectively, in the solution of AlCl$_3$; (b). From top to down r value was 2.5, 2.3, 2.0, 1.5, 1.0, 0, respectively, in the mixed solution of Mg:Al of 1:1 molar ratio.

Acknowledgments

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References

1. S. H. Han, W. G. Hou, C. G. Zhang, *et al.*, *J. Chem. Soc., Faraday Trans.*, **1998**, *94*, 915.
2. S. H. Han, C. G. Zhang, W. G. Hou, *et al.*, *Colloid Polymer. Sci*., **1996**, *274*, 860.
3. S. H. Han, C. G. Zhang, W. G. Hou, *et al.*, *Chem. J. of Chin. Univer.,* **1996**, *17*, 1785.
4. B. Alak, B. H. Daniel, *Inorg. Chem.*, **1992,** *31*, 3869.
5. D. Plee, F. Borg, L. Gatineau, J. J. Fripiat, *J. Am. Chem. Soc.*, **1985**, *107*, 2362.
6. J. Y. Bottero, J. M. Cases, F. Fiessinger, J. E. Poirier, *J. Phys. Chem.*, **1980**, *84*, 2933.

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