

INVESTIGATIONS ON ALUMINUM HYDROXIDE AND SOME INTERCALATION COMPOUNDS

Joachim Angelkort*, Manfred Knoll, Angelina Reichert
Intocast AG, Westpreußenstraße 30, 47809 Krefeld, Germany
Email: manfred.knoll@intocast.de, joachim.angelkort@intocast.de

Abstract

Aluminum hydroxide is used as a cementitious phase in the production of refractory linings. Fast heating of these types of linings can cause a spallation by abrupt water release. To facilitate a continuous evaporation of water during heating, the intergranular space of the microstructure of the linings is often enlarged by the use of organic aggregates possessing a bulky molecule structure. Insertion of ions into the crystal structure of aluminum hydroxide, a so-called intercalation, can possibly also influence the dehydration behavior of the linings. As the intercalation of aluminum hydroxide results into a widening of the distance between the $\text{Al}(\text{OH})_3$ layers, the amount of water molecules transferring between crystal and surrounding medium increases concomitantly with the insertion of ions.

Different intercalation compounds and their synthesis are described in the literature. While many of the corresponding articles report about the synthesis of intercalation products originating from insertion of lithium salts into the crystal structures of $\text{Al}(\text{OH})_3$, there is little information about the successful intercalation of magnesium salts. From economical point of view, however, an intercalation of magnesium salts would be more favorable than the use of lithium compounds. Recently, we were able to crystalize the new intercalation compounds $[\text{LiAl}_2(\text{OH})_6] \cdot \text{CH}_3\text{O}_2 \cdot n\text{H}_2\text{O}$, $[\text{MgAl}_4(\text{OH})_{12}] \cdot (\text{CH}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$ and $[\text{MgAl}_4(\text{OH})_{12}] (\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ by heating aqueous suspensions of aluminum hydroxide and metal salts. To determine the dehydration behavior of the synthesized samples, thermogravimetric measurements were carried out. X-ray diffraction experiments were evaluated to relate changes of the dehydration behavior with changes of the crystal structure accompanying the intercalation.

Introduction

The most prominent polymorphs of aluminum hydroxide are gibbsite, bayerite, doyleite and nordstrandite. In the crystal structures of these polymorphs, the hydroxide ions form close-packed double layers and define octahedral interstices of which two-thirds are occupied by aluminum atoms and the other third is empty. Differences in the crystal structures of aluminum hydroxide arise from different orientations of hydrogen bonds and different stacking sequences of the layers.

By a charge balanced insertion of cations onto the unoccupied octahedral sites and anions in the interspace between the double layers of gibbsite, a so-called intercalation, new compounds have been synthesized within the last decades [1, 2, 3, 4]. The intercalation of gibbsite by a lithium salt LiX with $\text{X}^- = \text{Cl}^-$, Br^- or NO_3^- e.g. results in a formation of charged double layers of $[\text{LiAl}_2(\text{OH})_6]^+$ enclosing the X^- anions [1]. Fig. 1 depicts the crystal structure of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$ for a underlying space group symmetry $P6_3/m$ together with the unit cell (solid dark lines in Fig. 1) as well as the atomic positions extracted from Ref. [1].

Instead of Li^+ cations also the small divalent cations $\text{M}^{2+} = \text{Mg}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} should be able to occupy the vacant octahedral sites and form $[\text{MAl}_4(\text{OH})_{12}]^{2+}$ layers [2]. Attempts to syn-

thesize the intercalation compound $[\text{MgAl}_4(\text{OH})_{12}](\text{NO}_3)_2$ were, however, not successful in a previous study [3].

Due to the different bonding of the hydrogen atoms, the polymorphs of aluminum hydroxide exhibit slightly different chemical reactivities and differ also in their inclinations to intercalate metal salts. To increase the chemical reactivity of their goods, industrial producers of high alumina binders often enlarge the specific surface area of their materials by an activation causing fine particle sizes combined with a low degree of crystallinity. In industry, activated alumina is generally produced by dihydroxylation of aluminum hydroxide. Although gibbsite is often mechanochemically activated before its use in the synthesis of intercalation compounds [2, 3, 5], no example of the application of activated alumina as reactant in the synthesis of intercalation compounds could be found in the literature.

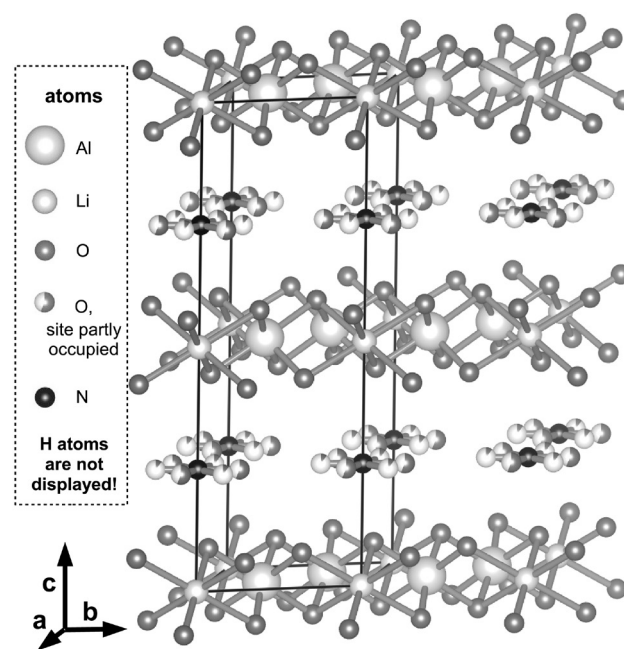


Fig. 1: Crystal structure of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$.

Experimental

Synthesis and sample preparation

The intercalation compounds were synthesized from slurries, which were prepared by mixing aqueous solutions of lithium or magnesium salts with hydratable activated alumina, by heating the mixtures for 5 hours at 50°C . The aqueous solutions of the metal salts were created by reacting lithium carbonate (Merck, 98.0%) or magnesium hydroxide carbonate (Merck, 98.0%) either with acetic acid (Merck, 99.9%) or nitric acid (Merck, 65.0%) and diluting the reaction products with deionized water to concentrations of $\sim 2 \text{ mol}\cdot\text{L}^{-1}$. 10 mL of the aqueous solutions containing the lithium salts were mixed with $\sim 3 \text{ g}$ of the alumina and 10 mL of the aqueous solutions containing the magnesium salts

were mixed with ~6 g of the alumina to account for an expected ratio of 1:2 pertaining the amount of lithium and aluminum atoms in the $\text{LiAl}_2(\text{OH})_6^+$ layers and an expected ratio of 1:4 for the amount of magnesium and aluminum atoms in $\text{MgAl}_4(\text{OH})_{12}^{2+}$ layers, respectively.

To perform X-ray powder diffraction measurements on the samples of the synthesized intercalation compounds, the samples were dried at room temperature and grinded in a mortar. Thermogravimetric measurements were carried out on the same samples and on a sample of activated alumina as well as gibbsite. To allow for a hydration of the activated alumina, about 4 g of the alumina was mixed with about 60 wt% deionized water and dried at room-temperature before it was used for the thermogravimetric measurement.

X-ray diffraction investigations

The formation of the synthesized intercalates was verified by measuring powder X-ray diffraction (XRD) patterns using a PANalytical X'pert³ diffractometer equipped with a Cu X-ray tube and a PIXcel^{1D} detector. For the measurements the acceleration voltage was adjusted to 40 kV and the beam current was set to 40 mA. The diffraction patterns were measured as θ - θ -scans in Bragg-Brentano geometry for 2θ ranging from 4 to 70 deg (Fig. 2). The measurements were recorded during a measuring time of about 90 minutes by rotating the X-ray tube and the detector continuously about the axis of the diffractometer.

Peak positions of the few broad peaks in the diffraction patterns of the synthesized intercalates were determined by profile fitting using the computer program Jana2006 [6] and starting values for the lattice parameters according to the indexation of peaks in the diffraction pattern of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$ in Ref. [1]. The refinements were accomplished by a full profile fit of the diffraction patterns using the Le Bail method. The calculations converged with a final value for the goodness of fit (GOF) of ~2.0 and a value for the agreement factor $R_p < 4.0$.

Thermogravimetric measurements

The temperature-dependent weight loss of the synthesized intercalation compounds was determined by heating small amounts of samples weighing about 0.5 g from room-temperature to 700°C using a thermogravimetric analyzer TGA 701 of Leco allowing a simultaneous heating of up to 19 samples. For the measurement the samples were heated with an average heating rate of 10°C per minute.

Results and Discussion

By reacting an aqueous solution of lithium nitrate with activated alumina, a reaction product formed which was identified through the measurement of an X-ray diffraction pattern to be a LiAl-layered double hydroxide compound [7]. As the diffraction pattern measured on the synthesized compound resembles the diffraction pattern of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$ published in Ref. [1], the reaction product probably constitutes a water-containing counterpart of the compound described in Ref. [1] possessing a chemical formula which can be expressed as $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$, with n standing for a not specified amount of water inherent in the compound.

The diffraction pattern we measured on the synthesized compound comprise strong peaks at ~10 and ~20 deg 2θ (Fig. 2) indicating that $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ is the prevailing reaction product of the synthesis. The successful synthesis of $[\text{MgAl}_4(\text{OH})_{12}](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ was indicated by measuring an X-ray diffraction pattern similar to the one of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ for a sample prepared from a mixture of an aqueous solution of magnesium nitrate and activated alumina (Fig. 2).

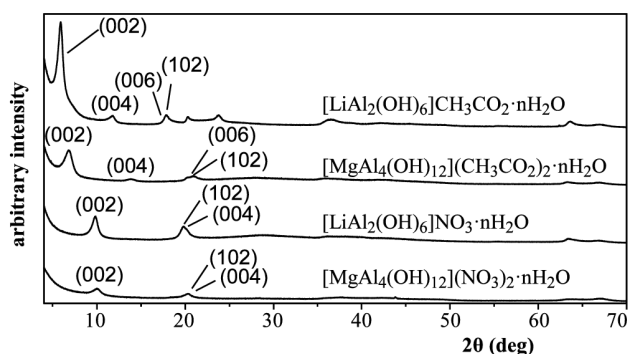


Fig. 2: XRD patterns measured on different intercalates.

Despite their common features, the diffraction patterns measured on the two synthesized compounds differ slightly in the positions of the peak maxima (Tab. 1), and peaks measured on $[\text{MgAl}_4(\text{OH})_{12}](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ are remarkably smaller and broader than the corresponding ones measured on $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$.

Tab. 1: Peak positions of reflections (002) and (102).

	2θ (deg)	
	(002)	(102)
$[\text{LiAl}_2(\text{OH})_6]\text{CH}_3\text{O}_2 \cdot n\text{H}_2\text{O}$	6.75	20.82
$[\text{MgAl}_4(\text{OH})_{12}](\text{CH}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$	7.09	21.39
$[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$	9.76	20.03
$[\text{MgAl}_4(\text{OH})_{12}](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	10.03	20.40

Also for samples which were synthesized by reacting aqueous solutions of lithium or magnesium acetate with activated alumina similar diffraction patterns have been measured. The peaks in the diffraction pattern measured on $[\text{LiAl}_2(\text{OH})_6]\text{CH}_3\text{O}_2 \cdot n\text{H}_2\text{O}$ are stronger than the corresponding peaks in the diffraction pattern of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$. Likewise, stronger peaks were found in the diffraction patterns measured on magnesium-containing intercalation compounds if the acetate was used for the synthesis. As the increase of a relative phase content in a sample results into higher intensity contributions of this phase in a measured X-ray diffraction pattern, higher peak intensities of the metal acetate-containing intercalates compared to the metal nitrate-containing intercalates probably points to a more completed intercalation reaction in the synthesis of the first-mentioned compounds. Compared to the nitrates, the acetates seem to possess a larger inclination to form intercalates, which is possibly a consequence of the size of the inserted anion. The insertion of larger anions accounts for a wider spreading of the double layers and allows for an easier intrusion of water molecules into the crystal structure resulting, in turn, in an increase of the reaction rate.

Besserguenev et al. reported in Ref. [1] the hexagonal lattice parameters of the dehydrated intercalation compound $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$ to be $a = 5.10917(8)$ Å and $c = 14.3738(3)$ Å. As these values were obtained for a water-free sample, and our samples probably have been containing a high amount of chemically bound water after they were dried at room-temperature, the lattice parameters of Besserguenev et al. were not suited as starting values for a profile fit of our measured data. Starting values for a profile fitting could be set, however, assuming that in agreement with the crystal structure of $[\text{LiAl}_2(\text{OH})_6]\text{NO}_3$ in Ref. [1] the strongest peak of the diffraction pattern is attributed to reflection 002 and that the second strongest peak results from partly overlapping intensity contributions of the reflections 102 and 004.

The lattice parameters of the synthesized intercalation compounds determined by profile fitting are compiled in Tab.2. The lattice parameter a of $[\text{MgAl}_4(\text{OH})_{12}](\text{CH}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$ is smaller than the

lattice parameter a of $[\text{LiAl}_2(\text{OH})_6]\text{CH}_3\text{O}_2 \cdot n\text{H}_2\text{O}$. Also for the intercalation compounds synthesized by reacting aqueous solutions of magnesium or lithium nitrate with activated alumina a smaller lattice parameter a can be found for the magnesium-containing intercalate (Tab. 2).

Tab. 2: Lattice parameters of the synthesized intercalates.

	a (Å)	c (Å)
$[\text{LiAl}_2(\text{OH})_6]\text{CH}_3\text{O}_2 \cdot n\text{H}_2\text{O}$	5.206(1)	26.160(4)
$[\text{MgAl}_4(\text{OH})_{12}](\text{CH}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$	5.079(1)	25.027(6)
$[\text{LiAl}_2(\text{OH})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$	5.863(1)	18.118(4)
$[\text{MgAl}_4(\text{OH})_{12}](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	5.785(1)	17.707(4)

Differences in the values of the lattice parameters determined for the magnesium- and lithium-containing intercalates could result from the slightly different effective ionic radii of Mg^{2+} ions (0.72 Å) and Li^+ ions (0.76 Å) for an octahedral coordination by oxygen atoms [8].

Due to different preferred oxidation states of magnesium and lithium atoms, a charge-balanced replacement of all Li^+ ions in a lithium-containing intercalates with Mg^{2+} ions would leave half of the octahedral sites originally occupied by Li^+ ions empty. The smaller lattice parameters of the magnesium-containing intercalation compounds compared to the lattice parameters of the lithium-containing analogs can therefore also be interpreted in terms of the presence of more unoccupied octahedral sites.

Interestingly, the lattice parameter a of the synthesized intercalation compounds seems also to be sensitive to the kind of anions embedded between the double layers. A substitution of nitrate anions against acetate anions affect a lowering of the lattice parameter a from 5.863 to 5.206 Å if the anions are enclosed between $[\text{LiAl}_2(\text{OH})_6]^+$ layers. For an accommodation between $[\text{MgAl}_4(\text{OH})_{12}]^{2+}$ layers, the same substitution of anions cause a change of the lattice parameter a from 5.785 to 5.079 Å (Tab. 2). The exchange of the nitrate anions against the more bulky acetate anions seems therefore to be accompanied not only by a widening of the interspace between the layers but also by a decrease of the lattice parameter a or, in other words, by an increase of the binding strength between the atoms of the double layers.

Thermogravimetric measurements were carried out to determine the relative weight loss of the synthesized intercalation compounds, of hydrated activated alumina and of gibbsite as a function of temperature (Fig. 3).

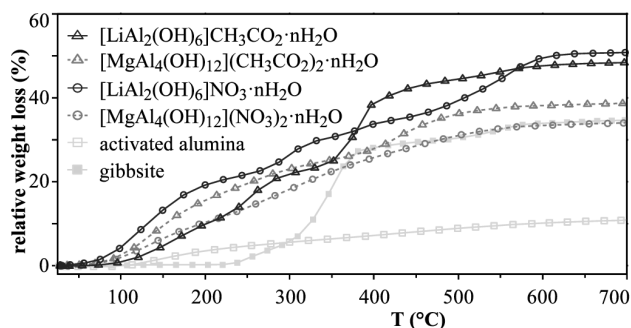


Fig. 3: Thermogravimetric measurements on different samples.

By heating of the samples from room-temperature to 700°C, hydrated alumina loses ~15 wt%, gibbsite loses ~35 wt%, and the intercalation compounds lose between ~35 to ~50 wt% (Fig. 3). While the relative weight loss of the activated alumina increases constantly from room-temperature to 700°C, the relative weight loss of gibbsite is found to be small for temperatures below 250°C

but increases steeply within a temperature interval ranging from ~250 to ~400°C. For temperatures above ~400°C the weight loss of gibbsite increases moderately.

As the weight loss of the intercalates results from both the evaporation of water and the release of other gasses produced during the decomposition, the curve of the weight loss is not an unbiased representation of the released amount of chemically bound water of the sample. Up to a temperature of about 300 to 400°C, however, the dehydration is probably the dominating process causing the weight loss. Thus, the constant increase of the relative weight loss of the intercalation compounds from ~100°C to the decomposition temperature of gibbsite can be attributed to the release of chemically bound water. Compared to the weight loss of gibbsite and activated alumina, the weight loss of the intercalation compounds is higher within this temperature regime evidencing a higher tendency of the intercalation compounds to release their chemically bound water at low temperatures.

Conclusions

Aqueous solution of lithium and magnesium salts can be reacted with activated alumina to synthesize intercalation compounds in which the anions are embedded between $[\text{LiAl}_2(\text{OH})_6]^+$ layers or $[\text{MgAl}_4(\text{OH})_{12}]^{2+}$ layers. In the diffraction patterns measured on samples of synthesized intercalation compounds stronger peaks were found for intercalates containing lithium and magnesium acetate than for intercalates containing lithium and magnesium nitrate, respectively. This observation possibly reflects the general tendency that the size of the intercalated anions affects the reactivity, e.g. by a widening of the interspace between double layers of not reacted crystal domains.

In contrast to gibbsite and activated alumina, the investigated intercalation compounds are subject to a comparatively high weight loss at temperatures between 100 and 400°C indicating a different behavior of these materials during heating. The large distance between the double layers in intercalation compounds probably allows for a more unhampered release of water during heating.

REFERENCES

- [1] Besserguenev AV, Fogg AM, Francis RJ, Price SJ, O'Hare D. Synthesis and structure of the gibbsite intercalation compounds $[\text{LiAl}_2(\text{OH})_6]\text{X}$ {X = Cl, Br, NO_3 } and $[\text{LiAl}_2(\text{OH})_6]\text{Cl} \cdot \text{H}_2\text{O}$ using synchrotron X-ray and neutron powder diffraction. *Chem. Mater.* 1997; 9: 241-7.
- [2] Williams GR, Moorhouse SJ, Prior TJ, Fogg AM, Rees NH, O'Hare D. New insights into the intercalation chemistry of $\text{Al}(\text{OH})_3$. *Dalton Trans.* 2011; 40: 6012-22.
- [3] Rees JR, Burden CS, Fogg AM. New layered double hydroxides prepared by the intercalation of gibbsite. *J. Solid State Chem.* 2015; 224: 36-9.
- [4] Thiel JP, Chiang CK, Poppelmeier KR. Structure of $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$. *Chem. Mater.* 1993; 5: 297-304.
- [5] Menzheres LT, Kotsupalo NP, Mamylova EV. Solid-state interaction of aluminium hydroxide with lithium salts. *J. Mater. Synth. Process.* 1999; 7: 239-244.
- [6] Petricek V, Dusek M, Palatinus L. Crystallographic Computing System JANA2006: General features. *Z. Kristallogr.* 2014; 229: 345-352.
- [7] Belskaya OB, Baklanova ON, Leont'eva NN, Gulyaeva TI, Likholobov VA. Mechanochemical synthesis of LiAl-layered hydroxides, precursors of oxidic supports and catalysts of the basic type. *Procedia Engineering.* 2015; 113: 91-7.
- [8] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* 1976; A32: 751-767.