

Chapter 2

Stearate intercalated layered double hydroxides: a comparison of methods

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Abstract

Calcined and uncalcined layered double hydroxides (LDH-CO₃) of the composition Mg₄Al₂(OH)₁₂CO₃·3H₂O were intercalated with stearate anions. Molten stearic acid (SA) in water was reacted with the carbonate anions of the interlayer. The presence of a surfactant, used to emulsify the SA and to disperse the LDH, did not significantly enhance the efficiency of intercalation, but prevented lump formation and facilitated the purification of the stearate intercalated LDH (LDH-SA) by removing unreacted SA during washing with water. Glycerol caused the removal of more carbonate anions possibly through intercalation of glycerolate anions, without facilitating stearate intercalation. Melting SA with LDH-CO₃ formed less LDH-SA than when the reaction took place in an aqueous medium. Reconstruction of calcined LDH in the presence of aqueous sodium stearate led to monolayer intercalation, whereas the methods entailing molten SA in aqueous media with LDH-CO₃ led to bilayer intercalation. Thermogravimetry was used for the first time to quantify the LDH-SA phase. The % mass loss in the temperature region 400-430 °C had a linear relationship to the relative amount of intercalated phase as determined by the internal standard method of XRD (I₅₀A/I_{9,3} A).

Keywords: layered double hydroxide, hydrotalcite, intercalation, stearic acid, glycerol, surfactant, calcinations, reconstruction, melt intercalation, infrared spectroscopy, thermogravimetry, X-ray diffraction



2.1. Introduction

Hydrotalcite is an anionic clay mineral with the composition Mg₆Al₂(OH)₁₆CO₃.4H₂O, and the layered structure of brucite [Mg(OH)₂], in which some of the Mg²⁺ ions are substituted by Al³⁺ ions. The presence of the Al³⁺ ions leads to a residual positive charge in the layers. This positive charge is balanced by anions such as CO₃²⁻, Cl⁻ and NO₃⁻ or organic anions in the interlayer [1]. For the CO₃²⁻ containing structure, the d-spacing of the (003) and (006) planes are 7,8 Å and 3,9 Å respectively [2]. A range of compositions are possible in terms of bivalent and trivalent cations and of their relative amounts. These types of compounds are generally referred to as layered double hydroxides (LDHs). They will be referred to as LDH-CO₃, LDH-Cl or LDH-SA (stearic acid), depending upon the anions residing in the interlayer region. Carlino [3] reviewed the different methods that are employed to intercalate carboxylic acids into LDHs. The relevant methods will be highlighted in the following paragraphs.

Due to the strong electrostatic and hydrogen-bond interactions, the carbonate anions in the interlayer are difficult to ion exchange. When the LDH-CO₃ is dehydroxylated and decarbonated at 400 - 500°C to form a layered double oxide (LDO) and subsequently reconstructed in an aqueous solution of a carboxylic acid (or its salt) or anionic surfactant, intercalation of the acid or the surfactant can be achieved. The hydrophobic interaction between the hydrocarbon chains, contribute to the stability of the intercalated product. The mechanism of this intercalation is believed to consist of the fast rehydration of the oxide and intercalation of OH⁻ anions, followed by the slow anion exchange of OH⁻ anions by the carboxylate anions [4].

Dimotakis *et al.* [5] developed a method of intercalating carboxylic acids or surfactants into LDH-CO₃ in the presence of glycerol as swelling agent, thereby improving the OH exchange in the interlayer. [Mg₆Al₂(OH)₁₆](OH)₂·xH₂O can be prepared from [Mg₆Al₂(OH)₁₆]CO₃·xH₂O by calcination and reconstruction in pure water (one volume equivalent) under nitrogen atmosphere. Upon addition of two volume equivalents glycerol, extensive swelling occurs. A glycerated phase, with basal spacing in excess of 40 Å, forms. In the presence of carboxylate anions, facile exchange of OH takes place



at room temperature. According to Hansen *et al.* [6], LDH-CO₃ can be swollen in glycerol liquid or glycerol vapour resulting in a basal spacing of 9,6 Å or 14,4 Å respectively. Subsequently, the CO₃²⁻ can be exchanged by dissolved nitrate, chloride or sulphate anions. It is believed that the glycerol in the interlayer decreases the electrostatic and H-bond forces acting on the carbonate, making the carbonate more exchangeable with other anions. Another possibility is that glycerolate anions (CH₂OH–CHOH–CH₂O⁻) are intercalated and exchanged [6].

Carlino *et al.* [7,8] developed a method in which molten sebacic acid (decane-1,10-dicarboxylic acid) and phenylphosphonic acid are intercalated into LDH-CO₃ in the absence of any solvents. The intimate mixture of the acid and LDH-CO₃ are heated slowly to above the melting point of the acid and kept there for 8 to 10 hours. Depending upon the molar ratio of acid to LDH, an intercalated phase or a salt (e.g. magnesium salt) of the acid formed. The products were biphasic because of the presence of unreacted LDH-CO₃ together with the intercalated phases [7,8].

Borja *et al.* [9] developed a method in which the Cl⁻ anions in LDH-Cl were ion-exchanged by the fatty acid anion in ethanolic solutions of lauric, meristic and palmitic acids. Literature procedures for the intercalation of specifically stearate anions into LDHs, mostly involve the anion exchange of Cl⁻ anions in LDH-Cl by stearate anions in aqueous solutions of sodium stearate under nitrogen atmosphere [10,11]. Depending on the amount of stearate present and the temperature employed, a monolayer or bilayer of stearate can be intercalated (Fig.1). The interlayer distance is about 32 Å for the monolayer and 52-53 Å for the bilayer [10,11]. Crepaldi *et al.* [12] developed a method of intercalating terephthalate ions into LDH-DS (dodecylsulphate) by salt formation between the intercalated DS⁻ and CTA⁺ (N-cetyl-N,N,N-trimethylammonium). The salt is extracted into chloroform.



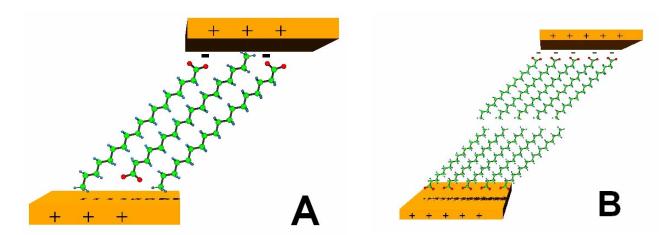


Figure 2-1 Monolayer (A) and bilayer (B) arrangement of stearate intercalated LDH (LDH-SA).

Organically modified layered compounds or clays such as LDH-SA can be used to form nanocomposites by being exfoliated within polymer matrices [13] or to protect and carry pharmaceuticals or genes [14] into cells due to its membrane-like structure or as stationary phases for chromatography [15]. Therefore, it would be beneficial to develop methods of intercalation that is time and energy efficient as well as environmentally friendly. In these respects, the starting reagent should be LDH-CO₃, which is easier to produce on large scale than, for example, the LDH-CI. Furthermore, the use of water, in stead of volatile organic solvents, low temperatures (no calcinations) and no N₂ atmosphere would be beneficial. These aspects are explored in this work.

The aim of this work was to intercalate SA into LDH-CO₃ with the formula Mg₄Al₂(OH)₁₂CO₃·3H₂O by a wide range of methods to form LDH-SA. The methods entailed reacting both LDH-CO₃ and LDO with SA in aqueous or ethanolic media or mixtures thereof. In the aqueous media the acidic SA is envisaged to react with and replace the CO₃²⁻ of the interlayer. To the best of our knowledge the use of SA and water to intercalate LDH-CO₃ has not been studied before. The effect of adding sodium dodecylsulphate (SDS) to the water was also tested. This surfactant-mediated method has, to the best of our knowledge, also not been studied previously. The use of 2:1 (v/v) glycerol/water mixtures with molten SA (similar to the method developed by Dimotakis



et al. [5] for nonanoic acid) was also tested as well as reacting the LDH-CO₃ with molten SA in the absence of solvents (similar to the method developed by Carlino et al. [7,8] for sebacic acid). Reconstruction of the LDO in the presence of aqueous sodium stearate was also performed. This research was aimed at determining the most efficient method for the intercalation of SA into LDH-CO₃ and developing thermogravimetry (TG) as a quick and easy tool for quantifying the LDH-SA phase.

2.2. Experimental procedure

2.2.1. Sample preparation

The layered double hydroxide (LDH) used in this study had the chemical formula $Mg_4Al_2(OH)_{12}CO_3$: $3H_2O$ (LDH-CO₃), and was supplied by Chamotte Holdings (Pty) Ltd, South Africa. The amount of crystalline water was determined from TG analysis. The mole ratio of Mg:Al was 2.01:1 as determined by XRF analysis (Appendix B). The particle size distribution as determined by the Mastersizer 2000 (Malvern Instruments) was d(0,1): 0,694 μ m; d(0,5): 5,062 μ m and d(0,9): 23,925 μ m. The theoretical anionic exchange capacity of this LDH-CO₃ was calculated to be 213 meq/100 g.

According to Itoh *et al.* [10] stearate anions can intercalate up to about 225% of the AEC. Therefore, stearic acid (SA, AR, 65-90%, Bio-Zone Chemicals) was used at 200% of the theoretical anionic exchange capacity (AEC) of the LDH. The intercalation of the LDH-CO₃ by SA was performed by 10 different methods (Table 2-1). A reference sample was also prepared in which no reaction took place (mixture of SA and LDH-CO₃ powders). The naming of methods in Table 2-1 are exemplified by the following: A sample or method name of *Calcined-SDS-water* refers to a sample or method in which LDH-CO₃, calcined at 500 °C, was reacted with SA in the presence of sodium dodecylsulphate (SDS) and water; the sample *Glycerol-water* was prepared by reacting the LDH-CO₃ and SA in the presence of a glycerol-water mixture. SDS was used to adsorb onto LDH surface to disperse it and to emulsify the SA. Deionised water, Glycerol (99%, UNILAB®), sodium dodecylsulphate (SDS, Empicol LZ/D, Akulu Marchon), sodium stearate (chemically pure, minimum 40%, UNILAB®) and ethanol (96% rectified, Dana Chemicals) were used. In methods where LDO was used 2 q of the



LDH-CO₃ was weighed, calcined at 500 °C for 2 h and the residue was added to the reaction mixtures. The mixtures were heated and stirred with a magnetic heater/stirrer at 70 °C for 2 h, unless specified as reacted for 24 h. All experiments were carried out in air in order to determine the efficiency of intercalation that one could expect under industrial conditions, where N₂ atmospheres would not be viable. Samples were washed with deionised water to remove excess SDS or glycerol; unreacted SA was not washed out. Mass yields of the LDH-SA were not determined because of the mixed nature of the product (containing SA, LDH-CO₃ and LDH-SA). Therefore, the relative amount of LDH-SA formed and unreacted LDH-CO₃ in the different methods was determined by XRD. Samples were filtered, except in the case of *SDS-water* methods in which the product was separated by centrifugation.

2.2.2. Characterization

2.2.2.1. Fourier Transform Infrared spectroscopy (FTIR)

A Perkin Elmer Spectrum RX I FT-IR System was used to scan the infrared transmittance through a KBr (Uvasol, potassium bromide, Merck) pellet 32 times at a resolution of 2 cm⁻¹. The averaged spectrum was background-corrected using a pure KBr pellet run under similar conditions. The pellets were prepared with approximately 2 mg of sample and 100 mg of KBr.

2.2.2.2. Thermogravimetry (TG)

15 mg of the powder sample was placed in a 70 μ l alumina pan. It was heated from 25 °C to 700 °C at a rate of 10 °C/min in air with no lid in a Mettler Toledo STAR^e System. The first derivatives of the thermogravimetric traces were used because it is more intuitive.



Table 2-1 Experimental details on the intercalation methods investigated.

Mother description and details on the intercalation methods investigated.				
Method name and details	Notes			
1. Water. 4,6 g SA, 2 g LDH-CO ₃ , 150 ml water.	Gelation after ca. 20 minutes			
SA is melted but not dissolved.	and later changed into lumpy			
Filter, dry and grind product.	agglomerates.			
2. Calcined-Water. 4,6 g SA, LDO*, 150 ml	Lumpy agglomerates formed.			
water. SA is melted but not dissolved.				
Filter, dry and grind product.				
3. Ethanol. 4,6 g SA, 2 g LDH-CO ₃ , 150 ml	No lumps formed.			
ethanol. SA is dissolved in ethanol.				
Filter and dry product. No washing.				
4. Ethanol-water. 2 g LDH-CO ₃ reacted with	Small globules formed (ca. 1			
4,6 g SA in a 1:1 v/v water/ethanol mixture.	mm diameter).			
5. SDS-water**. 4,6 g SA, 2 g LDH-CO ₃ , 150 ml	Well dispersed product.			
water, 2,5 g SDS. SA emulsified by SDS.				
Centrifuge, wash and dry product.				
6. Calcined-SDS-water**. 4,6 g SA, LDO*, 150	Well dispersed product.			
ml water, 2,5 g SDS. SA emulsified by SDS.				
Centrifuge, wash and dry product.				
7. Glycerol-water. 4,6 g SA, 2 g LDH-CO ₃ , 50	Spherical soft lumps formed.			
ml water, 100 ml glycerol. SA is melted within				
the liquid mixture, not dissolved.				
Filter, wash and dry product.				
8. Calcined-glycerol-water. 4,6g SA, LDO*, 50	A soft gel formed and			
ml water, 100 ml glycerol. SA is melted within	transformed into soft lumps.			
the liquid mixture, not dissolved.				
Filter, wash and dry product.				
9. Calcined-Na stearate-water**. LDO*	No lumps formation.			
reacted with 5,22 g sodium stearate (2 times				
AEC) dissolved in 150 ml water. 150 ml hot				
deionised water added after reaction and before				
centrifugation to retard rate of gelling of sodium				
stearate. Washed again with hot deionised				
water.				
10. Carlino melt. 2 g LDH-CO ₃ reacted with 4,6	Soft mixture showing channels			
g molten SA at 70 °C for 8 h. No solvents	through which CO ₂ gas			
present. In air.	escaped.			
11. Reference. No reaction. 2 g LDH-CO ₃	-			
powder mixed with 4,6 g SA powder.				
	I.			

^{*} Residue after 2 g of LDH-CO₃ was calcined at 500 °C in air for 2 h.

** 24 h reactions was also performed and denoted, for example, as SDS-water-24 h.



2.2.2.3. Powder X-ray diffraction (XRD)

The XRD analyses were done on a Siemens D500 X-ray system equipped with a 2.2 kW Cu long fine focus tube, variable slit and secondary graphite monochromator (to eliminate K_{β} radiation and reduce fluorescent radiation). The system is computer controlled using SIEMENS DIFFRAC Plus software. The goniometer was set to reflection mode. Samples were scanned from 1 to 40° 20 with Cu K_{α} radiation (1,5418 Å) at a speed of 0,02° 20, with a recording time of 2 s per step and generator settings of 40 kV and 30 mA. For quantitative XRD analyses the internal standard method [16] was used whereby 20 % m/m talc powder (< 10 micron, Sigma-Aldrich, 3MgO.4SiO₂.H₂O) was added to the obtained products. Sample preparation was done in standard sample holders by a single person in a repetitive way. Phases were quantified by determining the ratios of the intensities of the basal reflections to that of the 9,3 Å reflection of the talc.

2.2.2.4. Scanning electron microscopy (SEM)

Small amounts of the powder products or pristine LDH were placed onto carbon tape on a metal sample holder. The excess powder was removed by compressed air. A small piece of the gel-like mixture obtained during the *Calcined-glycerol-water* method was placed onto a carbon stub of approximately 5 mm diameter. It was frozen in a Reichert KF80 plunge freezer (Vienna, Austria). The frozen sample was dried in a custom built high vacuum freeze drier (Pretoria Technicon, South Africa). All samples were coated with chromium in a high resolution ion beam coater, Gatan model 681 (Warrendale, PA, USA) and studied with the JSM-6000F field emission scanning electron microscope (JEOL, Tokyo, Japan).



2.3. Results and discussion

Table 2-1 gives a summary of some of the observations made during the reactions.

2.3.1. Results and discussion of the different intercalation methods

2.3.1.1. Reference sample

During the thermogravimetric (TG) analysis of the reference sample, the stearic acid (SA) melted and intercalated to form the LDH-SA product with decomposition peak around 412 °C (Fig. 2-2). At the higher temperatures (during the temperature program), SA probably also reacted with the hydroxyl groups of the LDH layers, leading to the formation of thermally more stable products (decomposition temperatures of 441 °C and 473 °C, Fig. 2-2). Unreacted SA acid with a decomposition peak around 252 °C was present. The pure SA showed a decomposition peak at around 280 °C. The intercalation mechanism is similar to that of the method developed by Carlino *et al.* [7] in which the LDH and carboxylic acid powders were mixed and the acid allowed to melt. FTIR and XRD analysis showed the presence of only unreacted SA and LDH.

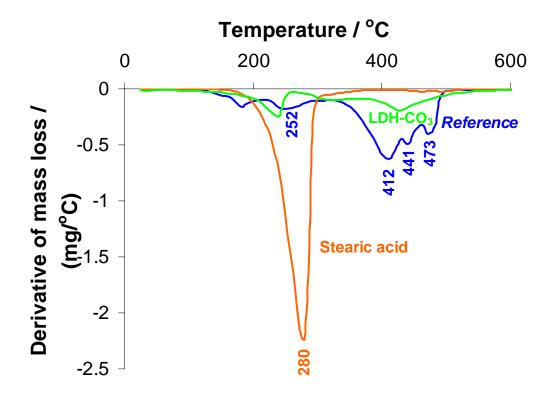


Figure 2-2 Derivatives of the thermogravimetric traces (DTG) of the LDH-CO₃, SA and the *Reference* mixture of LDH-CO₃ and SA, showing that SA intercalated during the analysis.

2.3.1.2. Ethanol and Ethanol-water methods

In pure ethanolic solution the intercalation could not take place because the SA was not ionized and, therefore, could not react with the carbonate of the LDH-CO₃ (Fig. 2-3, raw data in Appendix C). The amount of LDH-CO₃ present, were anomalously high with respect to the *Reference* sample (Fig. 2-4) because the SA stayed in solution and was not part of the solid product, leaving only a SA coating on the LDH-CO₃. The presence of 50% v/v ethanol (*Ethanol-water* method) did not reduce the efficiency of intercalation much (in terms of amount of LDH-SA formed) in comparison to the *Water* method (Fig. 2-3). The presence of the 50% v/v ethanol prevented the agglomeration that took place in the *Water* method. Agglomerated spheres of less than 1 mm diameter formed.

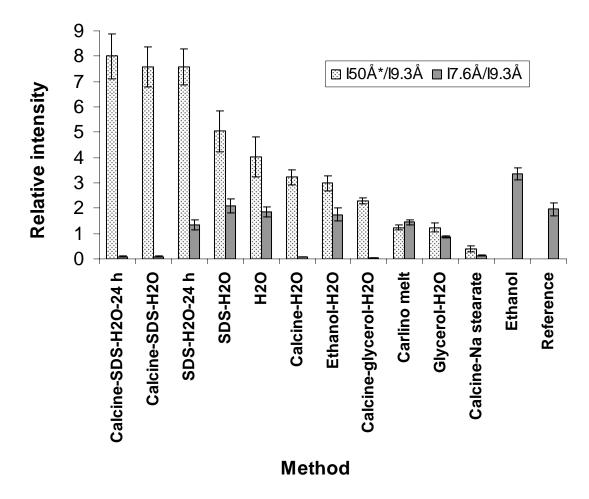


Figure 2-3 Relative amounts of the LDH-SA and LDH-CO₃ phases in the samples of different intercalation methods as determined by the internal standard XRD method. The raw data are given in Appendix C.

2.3.1.3. Glycerol-water and Calcined-glycerol-water methods

The relative amount of LDH-CO₃ phase diminished drastically in the presence of glycerol in comparison to the other methods (Fig. 2-3 and Fig. 2-4), and that without any calcination. The carbonate vibration at 1365 cm⁻¹ was drastically reduced and a small peak at 1384 cm⁻¹ remained. According to Hansen *et al.* [6] this could be attributed to the weakening of the H-bonds between the water and carbonate in the interlayer region by glycerol or even the intercalation of glycerolate anions. Therefore, one would expect more SA intercalation because of the removal of the carbonate counter-ions. However,

^{*} Reflection in the region of 50 Å.



less of the LDH-SA product formed in comparison to most methods (Fig. 2-3), a phenomenon which could be attributed to several factors. First, less SA was in the ionized state because the medium consisted of only about 33 % water. Second, FTIR spectra of these samples (Fig. 2-4) indicated a more amorphous structure (broad, unresolved peaks) in comparison to that of the *Water* method. The amorphous LDH-SA would be undetectable by XRD. The weak peak at 1725 cm⁻¹ (Fig. 2-4), also seen by Borja *et al.* [9] at 1720 cm⁻¹, could be attributed to the intercalation of the acid (COOH) itself.

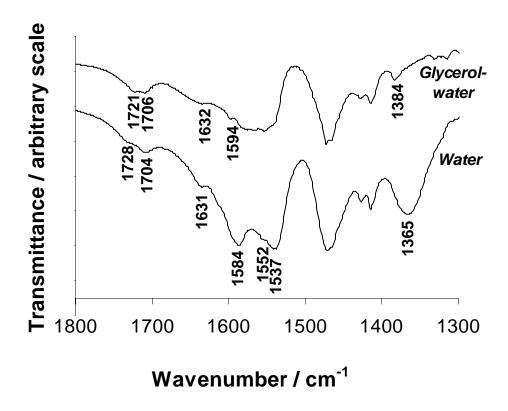


Figure 2-4 FTIR spectra of the *Water* and *Glycerol-water* methods, showing that the presence of glycerol caused the removal of carbonate from the LDH (large carbonate vibration at 1365 cm⁻¹ vs. small one at 1384 cm⁻¹) as well as a more amorphous arrangement of the stearate species (broad, overlapping carboxylate asymmetric stretching vibrations around 1550 cm⁻¹).

Stearate intercalated layered double hydroxides: methods and applications

LDH particles usually have sand-rose structures (Fig. 2-5 A). The particles consist of many intergrown smaller particulates which reduce the surface area [17]. This sand-rose structure broke down under the influence of the SA to form plate-like structures of large surface area (approximately 10 µm diameter, 200-500 nm thickness, Figs. 5 C and D), and gelling occurred. The thickening or "gelling" of the reaction mixture could be attributed to the house of cards arrangement of the plates (Figs. 5 C and D). The structure of the crystals looked much the same as the LDH-SA obtained by Itoh *et al.* [10] The formation of these gels seemed to depend upon the stirring conditions because in the case of the *Calcined-glycerol-water* method, the gel only formed during a large scale experiment (with overhead stirring) and not during the small scale experiment. When the gel of *Calcined-glycerol-water* was diluted and washed with water, dried and ground, neither the plate-like product, nor the sand-rose morphology of the original LDH persisted (Fig. 2-5 B).



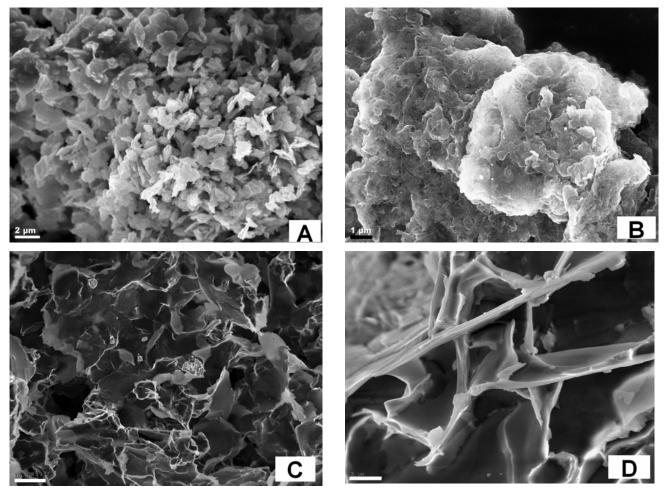


Figure 2-5 Scanning electron micrographs of the LDH-CO₃ showing the sand-rose microscopic structure (A), the powder product (B) and the gel of *Calcined-glycerol-water* (C and D). The bar in A is 2 μm, in B 1 μm, in C 10 μm and in D 2 μm.

2.3.1.4. Water, Calcined-water, SDS-water and Calcined-SDS-water methods

The FTIR spectrum of the LDH-SA obtained from the *SDS-water* method (Fig. 2-6) revealed the following: All the stearic acid reacted because the v(C=O) stretching vibration at 1702 cm⁻¹ was absent. The carboxylate (COO⁻) asymmetric stretching vibrations were at 1539 cm⁻¹, 1555 cm⁻¹, 1586 cm⁻¹ and 1635 cm⁻¹, which correlates well with the carboxylate asymmetric stretching vibrations (1542 cm⁻¹, 1557 cm⁻¹, 1589 cm⁻¹ and 1637 cm⁻¹) obtained by Borja *et al.* [9] for meristate intercalated Mg₃Al-LDH. The carboxylate asymmetric stretching vibrations are different from that of magnesium stearate (Fig. 2-6). The hydroxyl groups of the layers of the Mg₂Al-LDH are probably not



strong enough Brønsted bases to react with the SA (due to the Lewis acidity of the Al³⁺). Leaching of Mg²⁺ from the Mg₂Al-LDH used in this study (due to the presence of the acidic SA) is not expected because Hibino *et al.* [18] found that no leaching of Mg²⁺ cations took place in LDHs with Mg/Al ratio of 2 when treated with aqueous paramolybdate solutions (low pH), whereas substantial leaching took place in LDHs with Mg/Al ratios of 3 and 4. There is, furthermore, stoichiometrically not enough SA present for the salt (magnesium stearate) to form. The presence of the peak at 1362 cm⁻¹, attest to the fact that all the carbonate counter-ions did not react (Fig. 2-6). Longer reaction times and higher SA concentrations might be required for the complete conversion of the carbonate ions. The sulphate peak of SDS (1217 cm⁻¹, [19]) was not present, indicating that SDS did not co-intercalate (Fig. 2-6), probably because SDS has a different chain length from SA, the stearate intercalated LDH were more stable, the SDS was present in lower concentration than the SA, the SA alone satisfied the anionic exchange capacity and the SDS was not reactive toward the carbonate.

When LDHs are calcined at temperatures around 400 °C, a Mg-Al oxide with MgO-like structure forms [20]. MgO and SA are used to produce magnesium stearate [21]. Therefore, it was not surprising that the product of *Calcined-water* was similar to magnesium stearate in terms of the carboxylate asymmetric stretching vibrations (around 1575 cm⁻¹, Fig. 2-6) and the higher decomposition temperature (446 °C vs. 414 °C for *Water* method, Fig. 2-7). However, when SDS or glycerol was present in the system the products did not resemble magnesium stearate (Fig. 2-8). Therefore, these compounds adsorbed onto the basic sites of the LDO, protecting the carboxylic acid group of the SA from attack by the O²⁻ Lewis bases and the LDH-SA intercalates with lower decomposition temperatures formed (Fig. 2-8).

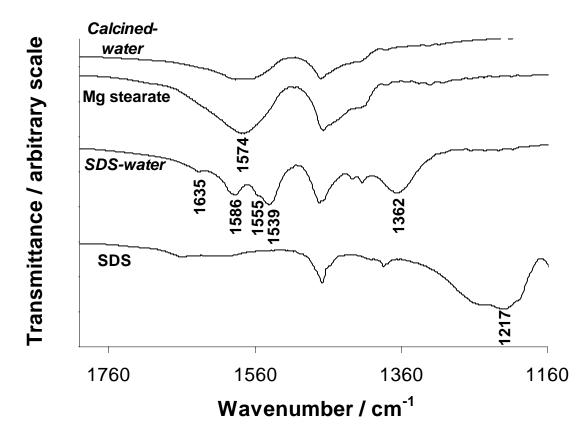


Figure 2-6 FTIR spectra of SDS, SDS-water product, magnesium stearate and Calcined-water product, showing that magnesium stearate did not form in SDS-water method, that SDS did not co-intercalate and that the product of Calcined-water were similar to magnesium stearate in the carboxylate asymmetric stretching vibrations (around 1575 cm⁻¹).

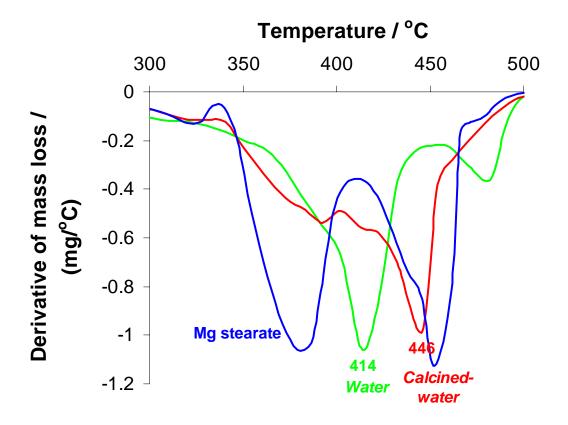


Figure 2-7 DTG traces of magnesium stearate, sample Water and sample Calcined-Water, showing that Calcined-water formed a product similar to magnesium stearate.

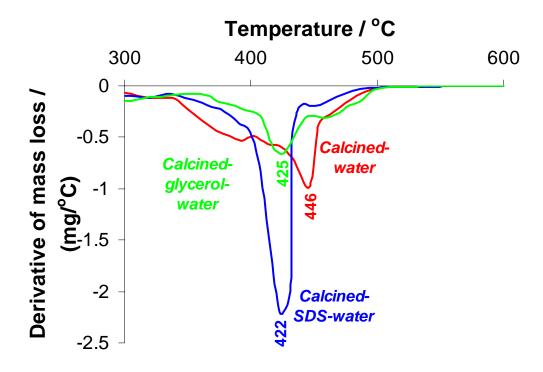


Figure 2-8 DTG traces of Calcined-water, Calcined-SDS-water and Calcined-glycerol-water, showing that the presence of SDS or glycerol protected the LDO from reacting with SA to form an Mg/Al stearate type salt; LDH-SA being the main product.

The reflections at 49,52 Å, 25,43 Å, 17,11 Å and 10,34 Å in Fig. 2-9 can be attributed to the bilayer intercalated LDH-SA. The pattern of the relative intensities of these 4 peaks (high, low, high, and low) is reminiscent of that obtained by Borja *et al.* [9] for the ion exchange of Cl⁻ in LDH-Cl by meristic acid in ethanol. Itoh *et al.* [10] attributed the reflection at 53 Å as the basal reflection of stearate intercalated LDH (bilayer) with the chains at approximately a 29° angle from the normal of the layers. This phase was present in the samples of all methods (with varying interlayer distances due to varying angles or degrees of interpenetration of the chains) except the *Ethanol* and *Calcined-Na stearate-water* methods. Monolayer intercalated LDH-SA was also present in sample *Calcined-SDS-water* as a minor phase (reflections at 30,35 Å and 15,43 Å, Fig. 2-9) but in none of the other methods (except *Calcined-Na stearate-water*). For SDS intercalation one would expect reflections at 26 Å, 36 Å or 47 Å depending on the mode of



intercalation [22]. The absence of these reflections (Fig. 2-9) indicates that no SDS intercalated, as was seen by FTIR analyses as well.

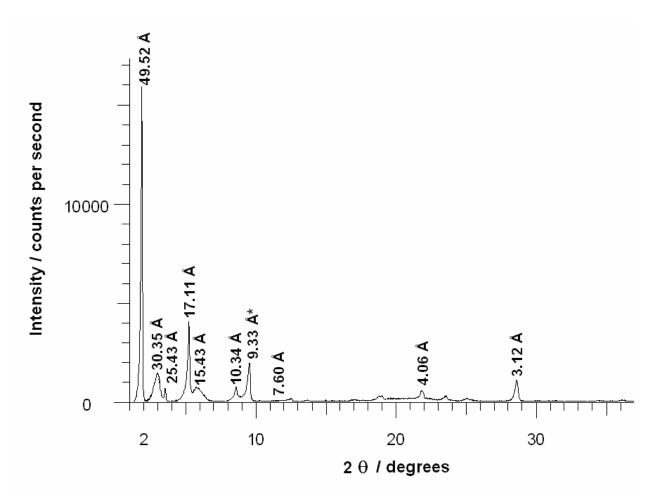


Figure 2-9 X-ray diffractogram of method *Calcined-SDS-water-24 h.* Reflections due to bilayer (49,52 Å, 25,43 Å, 17,11 Å and 10,34 Å) and monolayer (30,35 Å and 15,43 Å) intercalated LDH-SA were present.

Unreacted SA was removed together with the SDS during washing with water; consequently the product was enriched in the LDH-SA and unreacted LDH-CO₃ phases. This explains why there were (anomalously) somewhat more LDH-CO₃ present than in the reference sample (Fig. 2-3). The relative amount of LDH-CO₃, however, decreased from 2.1 ± 0.3 to 1.3 ± 0.2 when comparing a 2 h reaction with a 24 h reaction.

^{*} Reflection of internal standard (talc).



In a preliminary study it was found that the amount of surfactant did play a role in the amount of stearate that intercalated. For the same relative amounts of LDH and SA, the higher the SDS concentrations, the higher the yield (mass) of the LDH-SA after thorough washing with water and acetone. The internal standard method of XRD (Fig. 2-3) was not sensitive enough to capture these differences (compare *Water* and *SDS-water*). The correlation between the amount of surfactant and amount of stearate intercalation could possibly be attributed to the droplet size of the molten stearic acid as well as the surfactant adsorbing onto the LDH surface, preventing the side-reaction whereby the stearic acid reacts with the surface OH groups of the LDH.

Gelling occurred after 20 minutes of reaction in the *Water* method (as in *Calcined-glycerol-water* method), but in none of the other methods described in this paper. The gel was, however, too weak to withstand the preparation methods for SEM analysis, but it is believed to have the same microscopic structure as depicted in Figs. 5 C and D. Upon vicious shaking, the gel broke and the mixture could be stirred for the remainder of the time. Lumps of growing size started to form, which made magnetic stirring increasingly difficult (especially around and after 2 h of reaction), which possibly inhibited further diffusion of SA into the interlayer regions.

2.3.1.5. Calcined-Na stearate-water method

The carboxylate asymmetric stretching vibration region of sample *Calcined-Na stearate-water* looked almost identical to that of pure sodium stearate (Fig. 2-10). Therefore, at first it seemed as if no intercalation took place. However, reflections due to monolayer intercalation (31,90 Å and 15,69 Å) as well as a minor reflection at 45-48 Å due to bilayer intercalation were seen in XRD (Fig. 2-11). The decomposition temperature (T_{peak}) was lower (334 °C) than that of the bilayer intercalated products (about 420 °C). The reaction mixtures' tendency to gel makes the sodium stearate method less attractive.

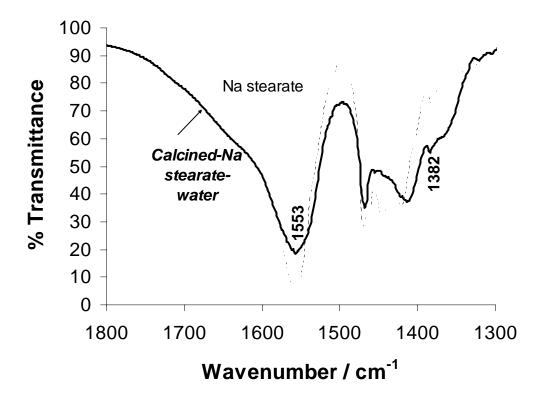


Figure 2-10 FTIR spectra of sodium stearate and sample Calcined-Na stearate-water, showing that the carboxylate asymmetric stretching vibrations of sodium stearate did not change much after intercalation (only some broadening seen).

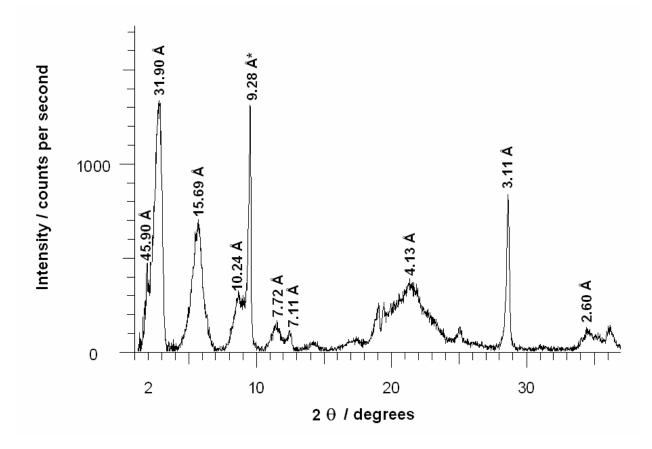


Figure 2-11 X-ray diffractogram of method Calcined-Na stearate-water-24 h. Monolayer intercalation with reflections at 31,90 Å and 15,69 Å were obtained together with a minor phase of near bilayer intercalation (45,90 Å).

2.3.1.6. Carlino melt method

In the case of the Carlino melt method less of the LDH-SA phase seemed to form even though more of the LDH-CO₃ disappeared (Fig. 2-3) with respect to the Water and SDS-water methods. One would expect, however, that more LDH-CO₃ have reacted because of the longer reaction time (8 h vs. 2 h). The low amount of LDH-SA could possibly be ascribed to the following factors: mixing was not as efficient as in the case of stirring in the presence of a solvent, the SA is less ionized due to the absence of water or the LDH-SA is less crystalline and could mostly not be detected by XRD. FTIR results also attested to the formation of a less crystalline product due to the broad overlapping

^{*} Reflection of internal standard (talc).



carboxylate asymmetric stretching vibrations. (Fig. 2-12) The relative heights of the peaks at 1550 cm⁻¹ and 1583 cm⁻¹ differed significantly from that of the other methods described in this work (Figs. 4 and 6, which correlated well with the relative heights seen by Borja *et al.* [9]). This is indicative that the carboxylates were present in different amounts in the different environments in comparison to the methods where water was present. There was also some unreacted SA (1706 cm⁻¹) left in the *Carlino melt* sample.

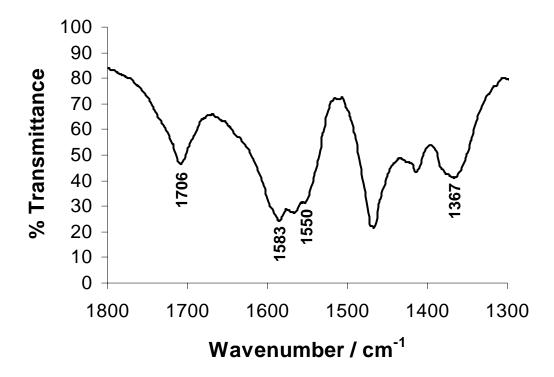


Figure 2-12 FTIR spectrum of the Carlino melt product showing different relative intensities of the carboxylate asymmetric stretching vibrations than the Water (Fig. 2-4) and SDS-water (Fig. 2-6) methods.



2.3.2. The effect of reaction time

The observed interlayer distances (basal reflections) ranged from 47-54 Å. There are indications that intercalated SA reached approached an equilibrium state with increasing reaction time because the interlayer distances decreased: Compare *SDS-water* with *SDS-water-24 h* as well as *Calcined-SDS-water* with *Calcined-SDS-water-24 h* in Table 2-2. The *Carlino melt* sample (which was reacted for 8 h) had an interlayer distance of only 47,04 Å. The solvents and other constituents may also have an effect on the observed interlayer distances (angle of the chains or extent of interpenetration of the chains). The decomposition peak temperature also increased with time (from about 420°C to about 438-446°C, Table 2-2). The higher decomposition temperatures can be due to the fact that the product reached a state closer to equilibrium (optimum Van der Waals interactions between chains) or reaction with hydroxyl groups might have occurred following the displacement of the carbonate anions by the carboxylates.

2.3.3. Correlation between TG and XRD data

The DTG curves of magnesium stearate and the intercalated LDH-SA phase cross each other at 400 and 430 °C (Fig. 2-7) It was thought that the mass loss between these two temperatures could be a quantitative measure of the amount of LDH-SA because it more or less excludes any Mg stearate like salts that might have formed. The mass loss of the uncalcined samples in the region 400-430 °C was indeed directly proportional to the relative amount of the intercalated LDH-SA phase as determined by the XRD internal standard method ($R^2 = 0.9923$, Table 2-3). The correlation was good because the basic LDH structure is unchanged. In Table 2-3 one can also see that the relative amount of LDH-SA that formed was dependent on the amount of water present in the medium. In the light of the time-dependent results given in Table 2-2, it is important to apply the TG quantization method only for samples reacted for the same time (e.g. 2 h) because the decomposition temperature (T_{peak}) shifted to temperatures above 430 °C at longer reaction times. When the calcination methods were added to the regression, the correlation coefficient decreased to 0,8563, because the reconstruction of the LDO in the presence of substances such as glycerol or SDS was affected due to adsorption onto the reforming crystals. When the Carlino melt and Calcined-Na stearate-water



methods were added to the equation, the correlation coefficient dropped to 0,7515, probably because the intercalation mechanisms at work are so different.

Table 2-2 Interlayer distances of samples prepared by different methods and peak temperatures (T_{peak}) for the decomposition of the LDH-SA phase.

	Interlayer	Interlayer	LDH-SA	
Method	distance of	distance of	decomposition T _{peak} /	
	bilayer / Å	monolayer / Å	°C	
Water	49,96-50,86	-	412-414	
Calcined-water	48,25-50,37	-	441-446	
Ethanol-water	49,52	-	418	
Ethanol	-	-	-	
SDS-water	48,94-50,86	-	418	
SDS-water-24 h	47,02	-	438	
Calcined-SDS-	54,48	30,74 (minor	422	
water	04,40	phase)	722	
Calcined-SDS-	49,52	30,35 (minor	446	
water-24 h	10,02	phase)	770	
Glycerol-water	48,25-49,94	-	431-438	
Calcined-glycerol-	48,25-49,97	-	408-425	
water	10,20 10,01			
Calcined-Na	48,25 (minor	31,90	334	
stearate-water	phase)	,	004	
Calcined-Na	45,90 (minor	31,90	328	
stearate-water-24 h	phase)	31,00		
Carlino melt	47,04	-	410	



Table 2-3 Correlation between XRD and TG data for the quantization of the LDH-SA phase.

Method	I ₅₀ Å/I _{9,3} Å *	% Mass loss from	Equation	Correlation
		400-430 °C		coefficient (R ²)
SDS-water	5,0	28	y = 4,3661x	0,9923
			+ 4,9846	
Water (100%	4,2	22		
water)				
Ethanol-water	3,0	17		
(50% water)				
Glycerol-water	1,1	10		
(33% water)				
Ethanol (no	0	5		
water)				
Calcined-SDS-	7,5	30	y = 3,3693x	0,8563
water			+ 7,5653	
Calcined-	2,4	22		
glycerol-water				
Calcined -	3,2	15		
Water				
Carlino melt	1,2	20	y = 3,3755x	0,7515
			+ 7,8328	
Calcined -Na	0,4	3		
stearate				

^{*} Relative amount of LDH-SA phase in region of 50 Å.

2.3.4. Recommendations for future work

It would be interesting to study the effect of varying the ratio of glycerol to water in the *Glycerol-water* method because the more glycerol present, the more carbonate will be removed, but the more water present, the more SA will intercalate due to ionization of the SA. A more thorough study of the time-dependent changes in interlayer distance and



basal reflection intensity should be conducted in future, for all methods described in this work. The shift in decomposition temperature should also be followed with time of reaction to learn more about the intercalation mechanism and product.

2.4. Conclusions

This article described a direct method for intercalating fatty acids into LDH-CO₃, due to a reaction between the carbonate and the ionized SA in aqueous media. In general, such a direct method of intercalation does not work with anions which are unreactive towards the carbonate. Even though the current experiments were carried out in air, virtually no LDH-CO₃ phase reformed in the cases where LDOs were used (Fig. 2-3). Therefore, the bilayer intercalated stearate anions has greater stability than LDH-CO₃, probably because of the stabilising effect of hydrophobic interactions between the chains [11,23]. Large scale production of the LDH-SA would, therefore, be easy because a N₂ atmosphere is not necessary.

Interestingly, XRD and FTIR analyses of the samples of these water-based methods remarkably resembled those obtained by Borja *et al.* [9] for the ion exchange of Cl⁻ in LDH-Cl and the fatty acid in ethanolic media. Therefore, as concluded by Borja *et al.* [9], the fatty acid intercalated in both the dissociated (COO⁻) and undissociated (COOH) form. Itoh *et al.* [10] also obtained bilayer intercalated LDH-SA by exchanging the Cl⁻ in LDH-Cl by stearate in aqueous sodium stearate solutions (24 h, 80 °C). It is clear from Fig. 2-11, however, that reconstruction of the LDO in the presence of aqueous sodium stearate led to the intercalation of a monolayer of stearate. Therefore, when using LDH-CO₃ as a starting reagent, molten SA in aqueous medium should be used to obtain bilayer intercalation.

The reaction mixtures of method *Water* and *Calcined-Water* could not be stirred for 24 h because large lumps (> 1 cm) tended to form, making stirring difficult. The lump formation did not drastically decrease the rate of LDH-SA formation within the first 2 h in comparison to the *SDS-water* and *Calcined-SDS-water* methods and it is unknown whether the rate of reaction is inhibited upon longer stirring times. Sodium dodecyl



sulphate (SDS) not only prevented this agglomeration, but also kept the unreacted SA in emulsion; therefore removing it from the final product. A purer LDH-SA end-product resulted with less effort. The surfactant-mediated methods of intercalation are, therefore, environmentally friendly because the SDS solutions should be recyclable and no volatile or flammable organic solvents (such as ethanol) are needed to free the product from SA. In the case of the Water methods the products were hard lumps, whereas in the surfactant-mediated methods the products were soft and easy to grind to a fine powder. Therefore, the surfactant played a role in terms of ease of stirring and ease of purification and grinding of the product and not in facilitating the reaction. The relative amounts of LDH-SA formed in the SDS-water-24 h, Calcined-SDS-water and Calcined-SDS-water-24 h methods (Fig. 2-3) were similar. The Calcined-SDS-water method was the most time efficient and the amount of LDH-SA formation seemed to have reached a plateau within the 2 hours. The SDS-water method should be tested at more time intervals to determine when a plateau is reached. The thermal history of the LDH-SA (whether it was calcined or not) could have an influence on the performance of the products within a given application and should be tested. When exposing the LDO to aqueous SA, however, a thermally more stable Mg/Al stearate type salt formed and much less of the desired LDH-SA in comparison to Calcined-SDS-water (Fig. 2-3). In the presence of glycerol, the CO₃² of the LDH-CO₃ were removed and probably replaced by glycerolate anions, without facilitating the intercalation of SA because the 2:1 glycerol/water does not allow ionization of as much SA as do pure water.

In this study it was found that TG could be used for quantification of the LDH-SA phase (especially for uncalcined samples) because the % mass loss in the region 400-430 °C correlated with the relative amount of LDH-SA phase as determined by XRD (internal standard method). Quantitative XRD needs more sample as well as the addition of an internal standard. Furthermore, sample preparation needs to be done meticulously and repetitively to prevent orientation of the LDH-SA crystals. If preferred orientation occurs, the intensity of the interlayer distance reflection is artificially enhanced [24] and the intensity could, therefore, be subject to erroneous quantification. TG analysis, on the other hand, requires only a few milligrams of sample and no special sample preparation



techniques to prevent preferred orientation of the crystals. The gradient of the linear equation (Table 2-2) indicated that the TG analysis was 3-4 times more sensitive than XRD to the amount of LDH-SA present.

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