chemengineering

Review

Preparation of Layered Double Hydroxides toward Precisely Designed Hierarchical Organization

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Abstract: Layered double hydroxides (LDHs) are a class of materials with useful properties associated with their anion exchange abilities for a wide range of materials' applications including adsorbent, catalyst and its support, ceramic precursor, and drug carrier. In order to satisfy the requirements for the detailed characterization and the practical application, the preparation of LDHs with varied composition and particle morphology has been examined extensively. The versatility of the preparation methods led LDHs with varied composition and micro/macroscopic morphology, which makes the application of LDHs more realistic. In the present review article, synthetic methods of LDHs are overviewed in order to highlight the present status of the LDHs for practical application.

Keywords: layered double hydroxide; co-precipitation; homogeneous precipitation; morphosynthesis; hydrothermal reaction; nanoparticles; mechanochemistry

1. Introduction

Layered double hydroxides (LDHs) are one of layered materials whose structure is composed of brucite ($Mg(OH_2)$) like layers stacked with interlayer anion. A part of the divalent cations in the brucite like sheet are replaced by trivalent ions, giving positively charged sheets, and to compensate the positive charge, anions occupy the interlayer space as shown in Figure 1. The chemical formula of LDH is expressed as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations in the sheet, respectively, x is the ratio of M^{3+}: (M^{2+} + M^{3+}), and A^{n-} is the interlayer anion. The flexibilities of the chemical composition (combination of various M^{2+} and M^{3+}) make LDHs useful for versatile applications. Accordingly, the preparation, characterization, and application of LDHs have been reported [1–9]. Application of LDHs in such areas as catalysts [10–15], catalyst' supports [16], electrode [17–20], ion exchanger/adsorbents [21], pharmaceutics [22–25], drug carriers [15,26–30], and so on has been proposed so far. In order to optimize materials' performances, efforts have been made to vary the composition as well as the particle morphology of the LDHs and their intercalates.

The particle size and size distribution are important parameters to affect materials' performances. For example, nanometer sized particles are useful for bio-related applications such as drug carrier [31–37]. Rheology of LDH suspension, which has been studied for the application as paints and for the preparation of polymer nanocomposites, is affected by the particle size [38–40]. Fabrication of LDH films has been investigated for electrochemical and photochemical applications [41–46]. These nanoscopic particle morphologies and micro/meso/macroscopic hierarchical architectures have been designed based on the sophisticated synthetic strategy and careful optimization of the reaction conditions. In the present review article, attention will be focused on the synthetic methods and their correlation with the characteristic features of the LDHs, in order to discuss the present situation of LDH preparation and application.

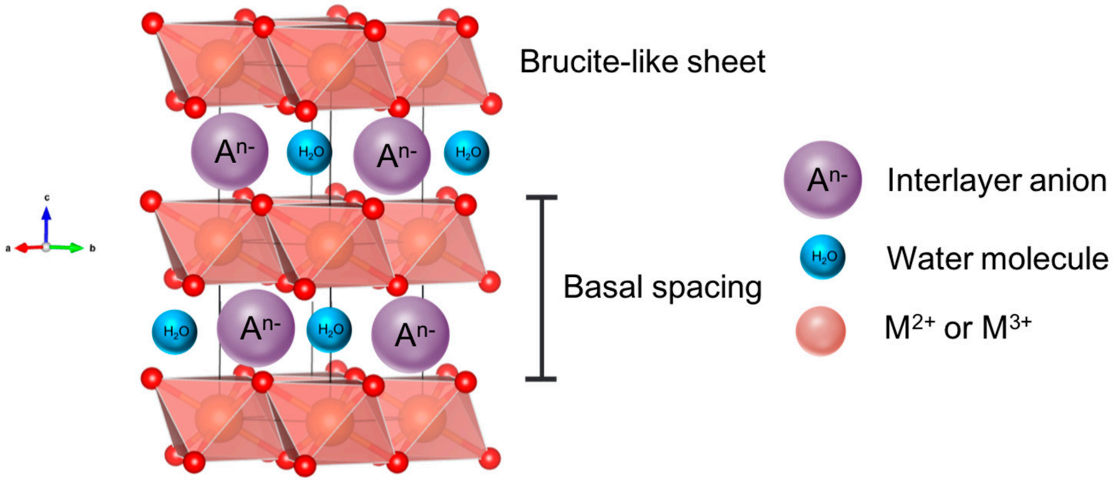

Figure 1. A schematic structure of layered double hydroxides.

2. Co-Precipitation from Homogeneous Solution

2.1. Co-Precipitation by the Addition of Base

Co-precipitation of LDHs from aqueous solutions containing divalent and trivalent metal cations by the addition of such bases as aqueous NaOH is a fundamental and the most common method for the synthesis of LDHs with various composition [47–49]. Co-precipitation has been used for the preparation of various type LDHs and their intercalation compounds. The obtained products were generally finite crystallites (nanometer scale) with broad particle size distribution, and aggregation of the particles were seen.

The precipitation has been done in several different sequences of mixing. Conventional titration, which a basic aqueous solution (NaOH, KOH, or NH_4OH) was slowly added to an aqueous solution (normally acidic) containing M^{2+} and M^{3+} ions until pH of a mixture reached to suitable value for the target LDHs, was commonly used [33,50–59]. Co-precipitation at low supersaturation with constant pH was done, where aqueous solution of metal salts and a basic solution were simultaneously added to a container containing deionized water to maintain the suitable pH for the precipitation of the target LDHs [60–66]. Precipitation at high supersaturation is also possible, where an aqueous solution containing M^{2+} and M^{3+} ions was directly added to the solution of NaOH [67–77]. LDHs thus formed were obtained as aggregates of nanometer size particles with hexagonal platy shape.

Since the change in pH is a dominant step for the LDH precipitation, the method of pH control has been examined. We have reported a way to raise pH of the starting solution of metal salts by using OH^- form of anion exchange resin as the base supply to prepare well-defined particles of LDHs successfully [78,79]. The synthetic procedures are as follows; aqueous stock solution of $MgCl_2 \cdot 6H_2O$ and aqueous solution of $AlCl_3 \cdot 6H_2O$ were mixed (Mg:Al ratio = 3:1). To this solution was added OH^-, which release from ion exchange resin. The OH^- was prepared by the titration of the original Cl^- form of ion exchange resin with NaOH solution. The mixture was continuously shaken at room temperature. During the reaction, pH increased as a result of the anion exchange of the resin between Cl^- and OH^-. After the reaction, the removal of ion exchange resin from suspension of product was easily by filtration. The TEM images (Figure 2) showed the finite size of the MgAl-LDH prepared using ion exchange resin as an alkaline source. Hexagonal platy particle with the lateral size of ca. 50 nm and narrow particle size distribution were observed. The suspension of the product was stable for several days due to the small particle size. The anion exchange resin has been used as an alkaline source for the preparation of ZnAl-, NiAl-, CuAl-, and CoAl-LDHs. The obtained products were platy particles with the lateral size less than 100 nm.

Li and his co-workers revealed that the effect of pH on the formation of the nitrate type NiAl-LDH using co-precipitation at constant pH method [80]. The results obviously showed that NiAl-LDH formed at pH 4 to 13 and larger amount of nitrate anions were found in LDH at lower pH value (pH = 4). Carbonate anions started to be incorporated into LDH at pH higher than 4 due to the higher solubility of CO_3^{2-} at relatively higher pH, indicating the effect of pH on the incorporation of anions in LDH.

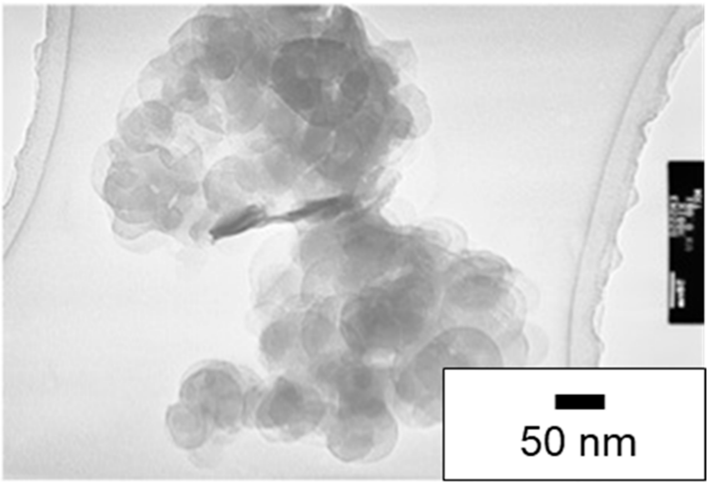

Figure 2. TEM image of nanometer size hydrotalcite prepared using ion exchange resin. Reproduced with permission from reference [81].

Recently, we have reported the syntheses of LDHs from concentrated solutions of the starting materials as an important option of bulk syntheses for the practical application [49]. The characteristics of the LDHs obtained and their synthetic conditions were summarized in Table 1. Briefly, the aqueous solution of mixed $MgCl_2{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ with the total metal concentration of 1.0 M (Mg:Al ratio = 3) (one of the highest concentration so far) was added by the 6.4 M NH_4OH solution to precipitate MgAl-LDH under atmospheric pressure and room temperature followed by aging. As a result of high concentration of starting metal solution use, large productivity of single phase chloride type MgAl-LDH (approximately 10 g from 160 mL solution) with the well-defined platy particles of ca. 50 nm were obtained without the need of inert atmosphere to suppress the formation of CO_3^{2-} type LDHs.

Table 1. Characteristics of the MgAl-LDHs obtained from concentrated solution of metal salts and the synthetic conditions.

Synthetic Condition									LDH Characteristic				Ref
$[Mg^{2+} + Al^{3+}]$ (M)	M^{2+}/M^{3+} Ratio	Base	[Base] (M)	Mixing Condition		Aging Condition			Product Amount (g from 100 mL)	Interlayer Anion	Particle Morphology		
				T (°C)	Atmosphere	T (°C)	Time (h)	Atmosphere			Shape	Size	
0.9	2	NaOH and Na_2CO_3	2.0	<35	Air	65	18	Air	5.9–7.1	CO_3^{2-}	Poorly dispersed unshaped aggregates	0.5 µm	[82]
	3			25		200		Air (closed container)	5.9		Poorly dispersed well-defined hexagonal plate	1 µm	[48]
						300			5.9		Well-defined hexagonal plate	15 µm	
1.0	3	NaOH	2.0	25	N_2		without aging		Not given	NO_3^-	Poorly dispersed spherical aggregates	Aggregates size 10–50 µm	[83]
										Cl^-			
										ClO_3^-			
			3.5	30	Air		without aging		Not given	SO_4^{2-}	Aggregates	>10 µm	[84]
			2.0							$Cr_2O_4^{2-}$			
	2	NaOH and Na_2CO_3	2.0	40	Air	150	24	Air (closed container)	Not given	CO_3^{2-}	Hexagonal aggregates	Not given	[85]
	3										Spherical aggregates	Not given	
	3	NH_3 gas	Not given	25	N_2		without aging		Not given	Cl^-	Poorly dispersed spherical aggregates	Aggregates size 10–50 µm	[83]
	3	NH_4OH	6.4	25	Air		without aging		9.7	Cl^-	Uniform platy particle	50 nm	[49]
						25	24	Air	10.6				
						80	24	Air	10.0				

The LDHs from co-precipitation were generally finite particles with broad particle size distribution, and aggregation of the particles was observed. Hence, various types of mixing conditions and post synthetic aging have been employed to increase the homogeneity of the product, to reduce the particle aggregation, and to increase the crystallinity.

Ultrasonication has been applied for the synthesis of LDHs. Zhao and his co-workers (2016) studied the effect of ultrasonication on the crystallite size and the aggregation of the particles by comparing with the LDHs prepared without sonication [86]. NiAl-LDH at the Ni:Al ratio of 3 was synthesized by the co-precipitation from aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, and NaOH and Na_2CO_3, which was done in the ultrasonication bath. The mixing was done under ultrasonication and mechanical stirring for 30 min, keeping the temperature at 50 °C. The precipitate was then aged at 50 °C for 10 h. As a comparison, a NiAl-LDH was synthesized by the co-precipitation without ultrasonication. The NiAl-LDH prepared under ultrasonication was an isolated disk-shaped particle. In contrast, the NiAl-LDH prepared without sonication was aggregates of thin plate with the lateral size of 50 nm as shown by the SEM images (Figure 3b,c) [86]. The effects of the reaction temperature on the crystallinity and crystallite size of the LDHs were examined. Climent and co-workers (2004) reported the preparation of MgAl-LDHs at the Mg:Al ratio of 3 by applying ultrasonication at different temperatures (0, 10, 25, and 50 °C). The increasing of the reflection intensity and the sharpness of diffraction lines were seen when increasing the reaction temperature as shown by XRD patterns (Figure 3a) [87].

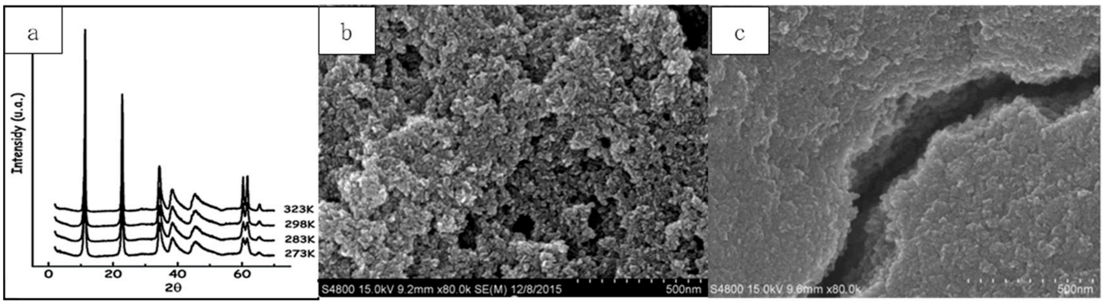

Figure 3. The variation of the XRD patterns (**a**) and the morphology (**b**,**c**) of NiAl-LDH prepared by coprecipitation with (**b**) and without (**c**) the ultrasonication. Reproduced with permission from reference [86,87].

The formation of nuclei and the crystal growth take place simultaneously leading to the wide size distribution. Zhao and his co-worker (2002) reported a method for the preparation of LDHs to obtain narrower particle size distribution by separating nucleation and aging steps using a colloid mill [88]. The synthetic procedures were as follows; an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at the Mg:Al ratio of 2, 3, and 4 and a basic solution of NaOH and Na_2CO_3 were simultaneously added to a colloid mill rotating at 3000 rpm and mixed for 2 min for nucleation. The resulting slurry was aged outside the colloid mill at 100 °C for 13 h. The precipitate was filtered, washed with deionize water, and dried at 100 °C for 24 h. The LDHs thus prepared were obtained as platy particles with the size in the range of ca. 60–80 nm. The particle size and shape of LDHs prepared using colloid mill were smaller and more uniform than the LDHs obtained without colloid mill as shown by the TEM images (Figure 4) [88]. The MgAl-, CuNiAl-, and CuNiMgAl-LDHs were also prepared and their particle size distribution was determined by laser light scattering to confirm the particle size distributions were narrower when colloid mill was used [88,89].

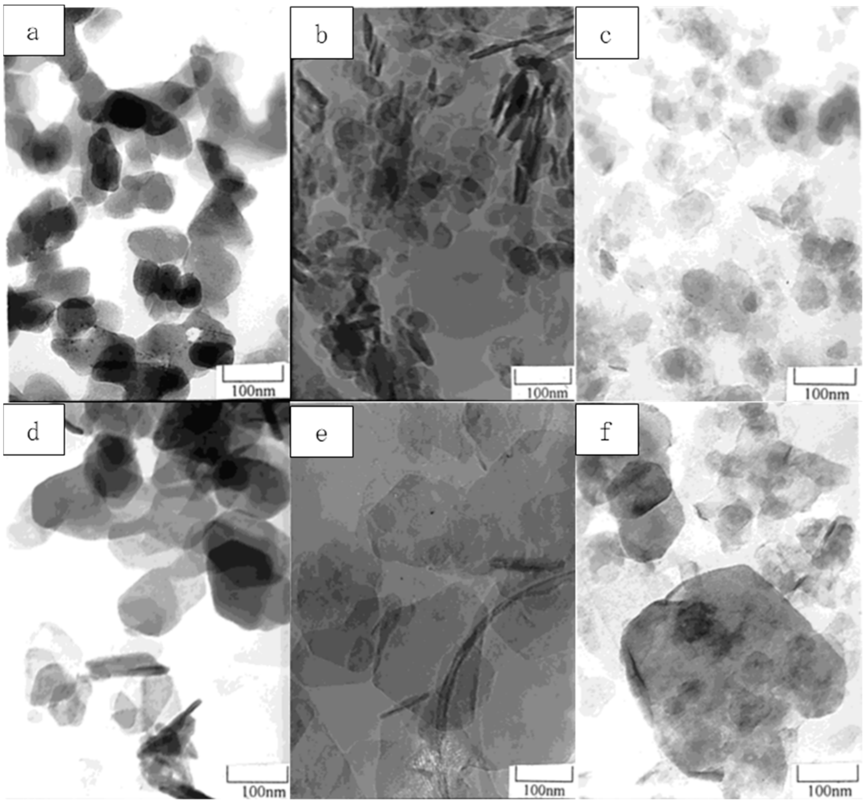

Figure 4. TEM images of MgAl-LDHs prepared by co-precipitation using colloid mill (**a**–**c**) and by conventional co-precipitation without colloid mill (**d**–**f**) (at the molar Mg:Al ratio of 2 (**a**,**d**), 3 (**b**,**e**), and 4 (**c**,**f**). Reproduced with permission from reference [88].

For the preparation of LDHs via co-precipitation in a batch, the mixing may not be homogeneous, which is a drawback to reproduce the products quality [90,91]. In order to overcome this drawback, flow reactor was used for the preparation of LDHs. Since the cross-section area of microreactor at the mixing point is in micrometer scale, rapid mixing was achieved by self-diffusion. The LDHs were prepared involving separate nucleation and aging under continuous process. Using a microreactor, MgAl-LDH (at the Mg:Al ratio of 2) was synthesized by simultaneous pumping an aqueous solution of metal salts and a basic solution at the flow rate of 20 mL/min through two inlets. The solid was separated, washed, and dried at 60 °C for 24 h. The MgAl-LDH thus formed were well-dispersed LDH, hexagonal platy particles with the lateral size of ca. 60–120 nm, as shown by the TEM image (Figure 5) [92].

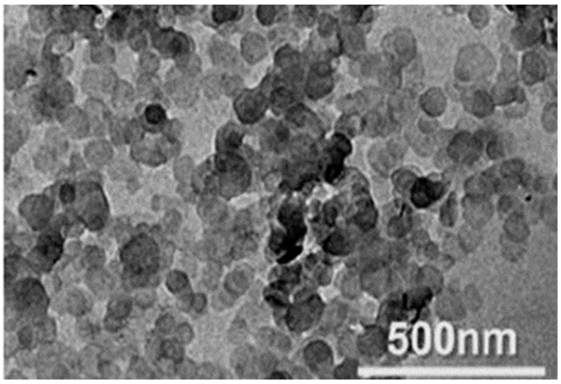

Figure 5. TEM image of a well-dispersed LDH prepared using microreactor under continuous process. Reproduced with permission from reference [92].

Post synthetic hydrothermal treatment was done to increase the particle size and crystallinity of the LDH. It has been reported that aging the LDH precipitates after co-precipitation under hydrothermal condition led LDHs with larger particle size than the one aged at room temperature [93]. The effects of the temperature and period of aging under the hydrothermal condition on the particle size and size distribution were studied [61]. MgAl-LDHs with the Mg:Al ratio of 2 was prepared by titration of aqueous metal salts solution with basic solution until the pH of mixture reached to 11. The resulting slurry was aged under hydrothermal conditions at 100 °C for 12–72 h and at 100–180 °C for 18 h to examine the effects of aging temperature and periods on the morphology of LDHs. As shown by the SEM images (Figure 6a,b), higher temperature and longer periods led the products with well-defined particle; the particle size was controlled in the range of ca. 115–340 nm by the reaction temperature and in the range of ca. 85–120 nm by the reaction periods [61].

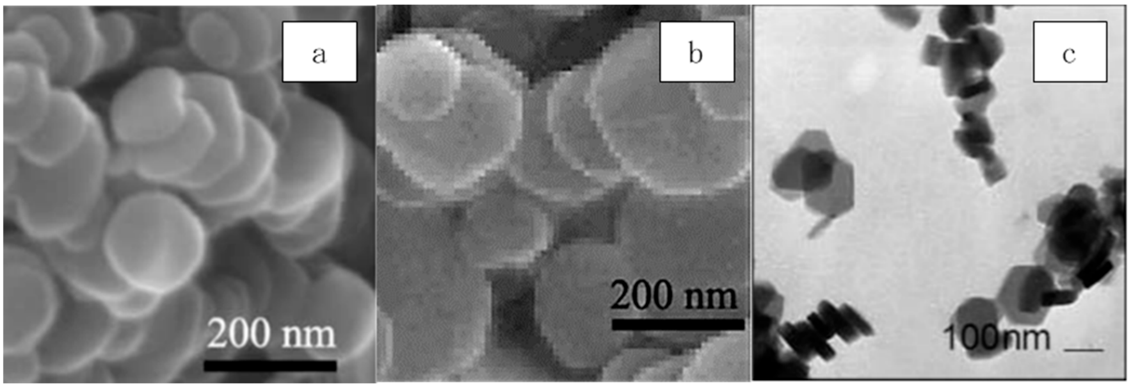

Figure 6. SEM images of LDHs prepared by coprecipitation under hydrothermal condition; aging at 100 °C (**a**) and 150 °C (**b**) for 48 h; and under microwave irradiation; aging at 100 °C (**c**) for 5 h. Reproduced with permission from reference [61,94].

Microwave heating has been applied to synthesize LDHs [94,95]. Benito and co-workers (2007) reported that the shape and average sizes of the LDHs, which were aged under hydrothermal condition at 100 °C for 24 h, were similar to the LDHs aged under microwave irradiation at 100 °C for 3–5 h as shown by the TEM image (Figure 6c), showing rapid heating by the microwave irradiation [94].

2.2. Homogeneous Precipitation

Homogeneous precipitation using the decomposition of urea at elevated temperature is a well-known method to obtain well-defined inorganic particles [96]. During the heating, urea hydrolyzes to give carbonate and ammonium ions, resulting in the homogeneous pH raised, which often results in the monodispersed particles of hydroxides and carbonates. The urea approach has been used to prepare LDHs with narrower particle size distribution compared to those of the LDHs prepared by titration [4,97–103]. The LDH prepared using urea method has been used as the host material for the organic anions' incorporation through ion exchange reaction [104]. Hexamethylenetetramine has also been used to make solution basic for LDH precipitation [105].

We have reported the preparation of large platy particles of LDH with the size of 40 μm by applying urea method under hydrothermal conditions [106,107]. As an example, the XRD pattern and the SEM image of hydrotalcite prepared by the hydrothermal reaction using urea are shown in Figure 7. We have also revealed the successful control of the particle size distribution using the hydrothermal reaction in aqueous alcohol [108,109].

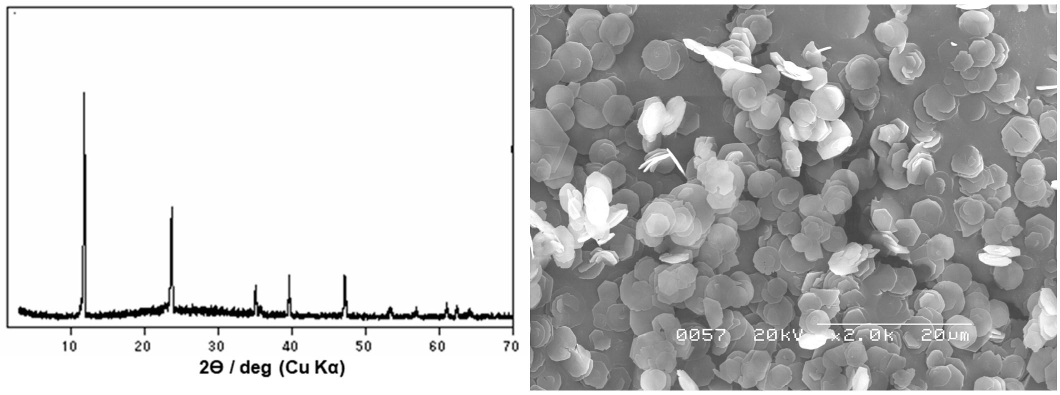

Figure 7. XRD pattern and SEM image of MgAl-LDH prepared by the homogeneous precipitation method using urea. Reproduced with permission from reference [81].

As an example, synthetic procedure of CoAl-LDHs is described here. Aqueous stock solutions of $CoCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and urea ($(NH_2)_2CO$) were mixed at a molar Co:Al:$(NH_2)_2CO$ ratio of 2:1:10. The aqueous mixture (homogeneous solution) was allowed to react under a hydrothermal condition. The precipitates obtained showed obvious pink colored and the main product was CoAl-LDH as determined by XRD, TG-DTA, and IR results [110,111]. The particle size was successfully controlled by the reaction temperature and period. It was found that larger particles formed by the reactions at lower temperature and longer reaction period owing to the slow urea hydrolysis at lower temperature, which was expected to suppress the formation of nuclei in the solution. When the reaction was conducted at 60 °C for 100 days, particles with a lateral size larger than 40 μm were successfully obtained, as shown in the SEM image (Figure 8).

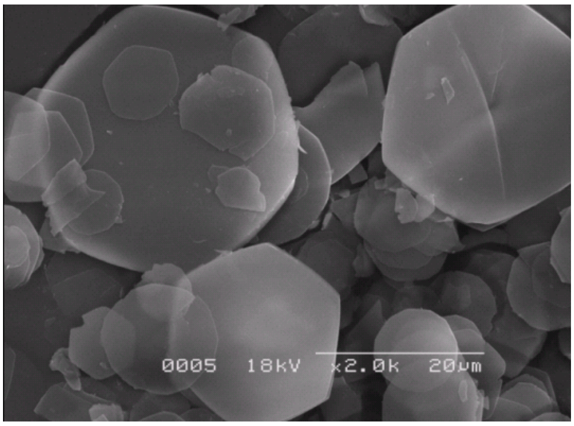

Figure 8. SEM image of a large platy particle of CoAl-LDH. Reproduced with permission from reference [81].

The particle size and size distribution of CoAl-LDHs were controlled by adding alcohols (ethylene glycol and glycerol) to the starting solution mentioned above [108]. The LDHs prepared by adding glycerol gave the narrower particle size distribution [108], so that the effects of the synthetic conditions on the particle morphology were also examined for the preparation of LDH from aqueous glycerol solution. Hexagonal platy particles of CoAl-LDH were obtained when glycerol/water ratio was 1 g/40 mL, and the reaction temperature was controlled at 80 °C. Average particle diameters were 3.8, 9.3, and 10.1 μm with the coefficient of variation (CV) values of 22.5%, 23.3%, and 24.7% when the heating time was 1, 2, and 7 days, respectively. It was shown that pH after the reaction increased with prolonged periods (pH = 6.09, 6.27, and 8.50, for the reactions for 1, 2, and 7 days, respectively), resulting in higher product yields. The product yield and the particle size suggested the particle growth was completed within a few days by the reaction at 80 °C.

It has been reported that urea hydrolysis rate depends on the reaction temperature. Therefore, the temperature is one of the crucial parameters to determine the particle size. It is known that the urea decomposition rate increased by ca. 200 times when increasing the temperature from 60 to 100 °C [112]. Larger particle size of LDHs could be obtained from slow urea hydrolysis rate, where the limited number of nuclei formed and grew. The particle prepared at 80 °C for 1 day (pH = 6.09 after the reaction) was larger than that prepared at 100 °C for 1 day (pH = 8.50 after the reaction).

The effect of glycerol amount added into the metal precursor solution on the particle morphology was investigated for the synthesis at 100 °C for 1 day. When the glycerol/water ratio was 0 and 1 g/40 mL, the products were hexagonal platy morphology. When the glycerol/water ratio was 10 g/40 mL, the products were circular plate. Shapeless and stick-like particles of approximately 1 μm length were obtained besides the circular plate, which is the main product, when the glycerol/water ratio of 15 or 20 g/40 mL were used. The difference between hexagonal plate and circular plate is worth discussing from the viewpoints of crystal growth mechanisms and the properties. The average particle size of the products decreased with increasing the glycerol/water ratio, while the particle size distribution of the products did not change.

After the reaction at 50 °C for 150 days, circular platy particle of CoAl-LDH with the average diameter ca. 1 μm, which was smaller than that (38 μm) of the product prepared without glycerol in the starting solution [107], was obtained [109]. A SEM image is shown in Figure 9. Very narrow particle size distribution (ca. 13% coefficient of variation) was achieved for the product prepared with glycerol heating at 50 °C for 150 days.

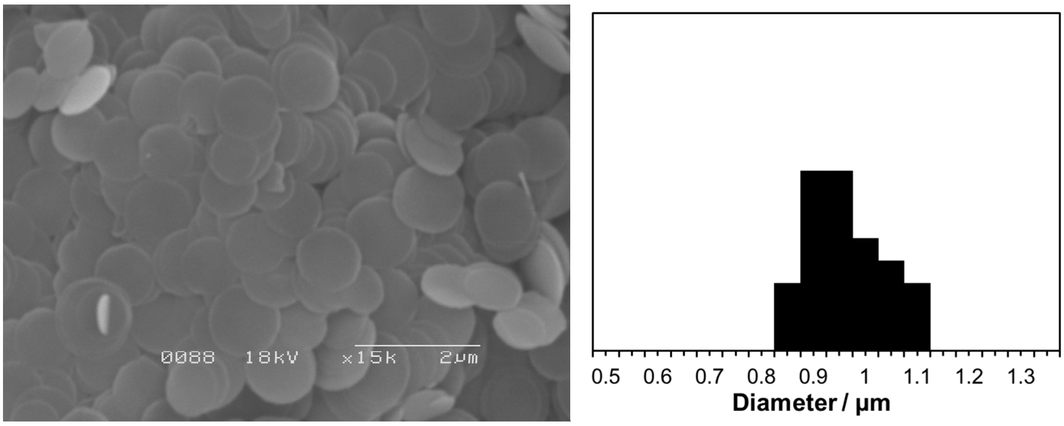

Figure 9. SEM image of a CoAl-LDH with narrow particle size distribution. Reproduced with permission from reference [81].

2.3. LDH Precipitation from the Solution Containing Additives

The synthesis of LDH in surfactant solution and emulsion has been conducted [113–117]. A surfactant was dissolved in water-oil (organic solvents-water) and form reverse micelles, where the hydrophobic chains pointing out into the oil phase and water droplets were entrapped in the reverse micelles. Chemical reactions were allowed to occur within the reverse micelles (water droplets) due to the higher solubility of starting materials in water, so that the reverse micelles act as microreactor. The effects of water content on the morphology of MgAl-LDHs were examined by Hu and co-workers (2007). The synthetic procedures were as follow; a basic solution was added dropwise in emulsion with different water/surfactant fractions (12, 24, 36, and 48), containing $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}6H_2O$, sodium dodecyl sulfate, 1-butanol and isooctane. After mixing and aging, the precipitate was refluxed in an ethanol/water mixture, and then, washed with acetone in order to remove the surfactant. The multilayer structures in the products were observed at the water/surfactant fraction of 36 and 48, because the micelles size increased when increasing the water/surfactant fraction. In contrast, the particles prepared at the lower water/surfactant fraction were round platy-shaped with the particle size in the range of 40–80 nm as shown in Figure 10 [115].

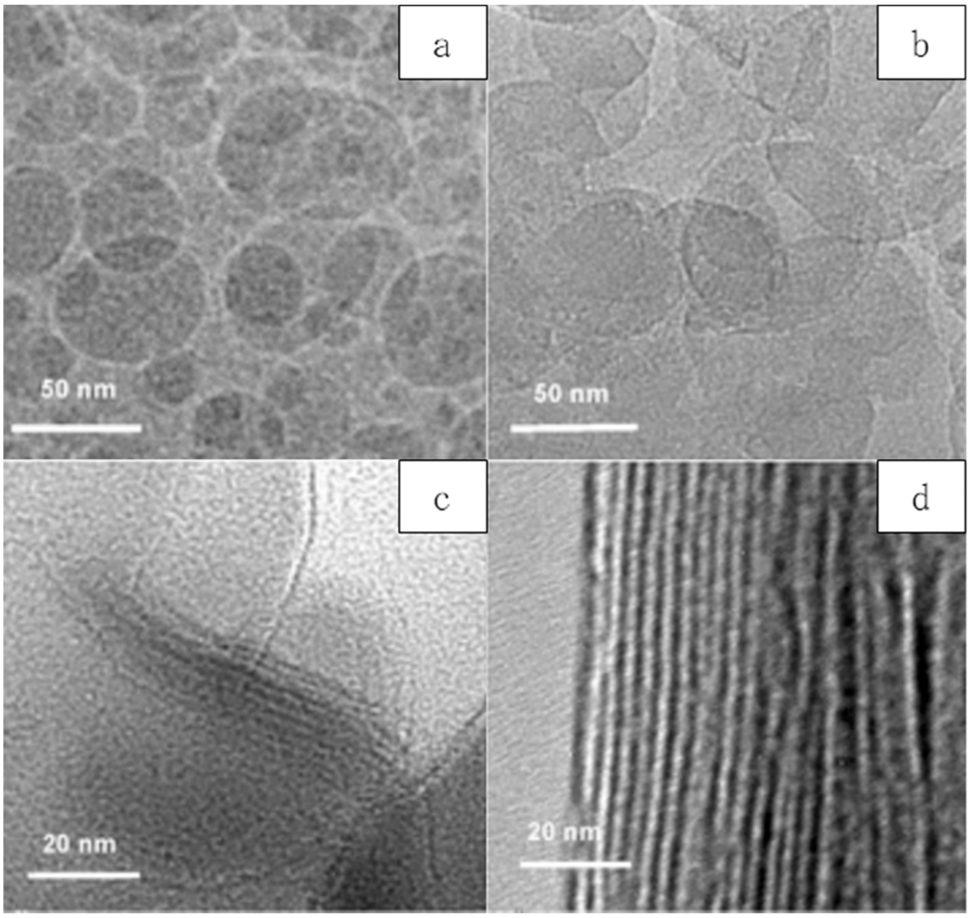

Figure 10. TEM images of LDHs synthesized in reverse micelles with the water/surfactant fraction of 12 (**a**), 24 (**b**), 36 (**c**), and 48 (**d**). Reproduced with permission from reference [115].

3. Preparation from Slurry of Metal Oxides/Hydroxides

In addition to the preparation of LDH from homogeneous solution, we have developed another simple synthetic method of LDHs, where oxides and hydroxides were used as the source. By using magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite), the MgAl-LDH-deoxycholate intercalation compounds were successfully prepared [118]. The selectivity of bulky and monodentate deoxycholate anion as the interlayer anion of LDH was very low, and other synthetic methods, conventional co-precipitation, anion exchange, and reconstruction were not applicable for the syntheses so that the hydrothermal synthesis starting from magnesium hydroxide (brucite) and aluminum hydroxide (gibbsite) was developed to successfully prepare deocycholate-LDH intercalation compounds. The method is an easy and environmentally friendly method and, later on, was applied for the preparation of a series of LDHs with different compositions and properties.

The hydrothermal synthesis of LDHs from aqueous suspension of magnesium hydroxide and aluminum hydroxide was used for the synthesis of the sulfide containing MgAl-LDHs. Thioacetoamide was used as the sulfide source for the study [119]. The reaction is as follows; brucite and gibbsite powders were mixed with an aqueous stock solution of thioacetoamide with vigorous stirring. The mixture was transferred into a Teflon-lined autoclave and heated at 150 °C for 1 day. Light green colored precipitates were obtained by the reactions. During the hydrothermal reactions, magnesium hydroxide and aluminum hydroxide were thought to be dissolved and subsequently precipitate as LDH with containing polysulfide anions (S^{2-} and S^{3-}). The polysulfide anions were thought to be derived from the decomposition of thioacetoamide. The product with blue color corresponding to the S^{2-} and S^{3-} ion turned to colorless when the sample was heated in air at 120 °C or stored for several days, indicating that the occluded polysulfide anions were oxidized to sulfate anion by atmospheric oxygen. The thermal analyses in air showed an exothermic reaction accompanying a weight gain at around 150 °C, and the infrared spectrum showed an appearance of absorption bands ascribable to sulfate ($SO_4{}^{2-}$) anion, showing the oxidation of the sulfide anions to sulfate anion as schematically shown in Figure 11.

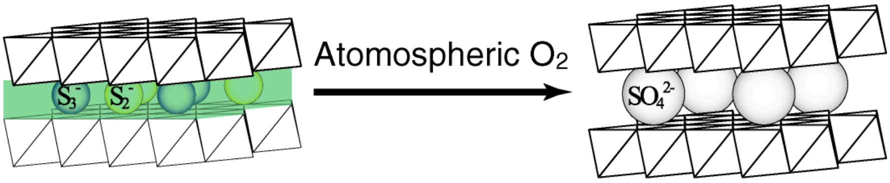

Figure 11. A schematic structure of polysulfide containing MgAl-LDH. Reproduced with permission from reference [81].

The synthetic method was extended for the preparation of ZnAl-LDHs. Benzenesulfonate was used as the interlayer anion to be directly incorporated into the interlayer space of the LDH by the hydrothermal reactions of aqueous suspension of zinc oxide and gibbsite [120]. The synthetic procedure of ZnAl-LDH containing benzenesulfonate (abbreviated as BS) is shown below; first, zinc oxide, gibbsite powders, and benzenesulfonic acid were mixed in distilled water with vigorous stirring. The aqueous mixture (slurry) was transferred into a Teflon-lined autoclave and heated at 150 °C for 1 day. After the hydrothermal reaction, the precipitate was separated by centrifugation, and the formation of ZnAl-LDH containing BS in the interlayer space was confirmed by XRD, IR, TG-DTA. It was found that the hydrothermal reaction in an absence of BS exhibited the remaining of starting materials (zinc oxide and gibbsite), suggesting the crucial role of BS for the incorporation of guest species as well as to dissolve zinc oxide and gibbsite. BS made the solution pH lower, so that the dissolution of zinc oxide and gibbsite was promoted. Prolonging the reaction time and conducting the reaction at higher reaction temperature were suggested to be a way to eliminate the remaining starting materials.

The hydrothermal treatment of gibbsite and magnesium oxide (MgO) at 180 °C, was reported for the preparation of LDHs by applying the similar synthetic condition [121]. Later on, Xu and Lu (2005) reported the LDH formation by the hydrothermal treatment of aqueous slurries containing MgO and Al_2O_3 at 110 °C [122]. The hydrothermal treatment at a temperature ranging from 100, 150, 180, and 240 °C were examined in situ using synchrotron irradiation [123]. More recently, ZnAl-LDHs containing chloride anion was synthesized from ZnO and $AlCl_3 \cdot 6H_2O$ by the hydrothermal treatment at 150 °C for one day [124]. These reactions are simple and versatile methods for the synthesis of LDHs. Nonetheless, the method is limited for the preparation of chloride, carbonate, and nitrate anion intercalated LDHs besides our reports on the preparation of deoxycholate [118] and polysulfides [119] containing LDHs.

4. Mechanochemical Syntheses

Preparation of LDHs by the solid-state reaction is worth investigating as an alternative to solution and slurry base methods. Mechanochemical synthesis, in which mechanical energy is used to induce the chemical reaction for the formation of material have been a topic of interest [125–132]. Mechanical forces such as compression, shear, and friction are used to induce the reaction by simply grinding the starting materials with mortar and pestle, or by using mill (ball mills and planetary mills). LDHs have been synthesized by several mechanochemical methods, and we recently summarized the reactions (Figure 12) [133]. In this section, examples of the mechanochemical syntheses of LDHs will be introduced.

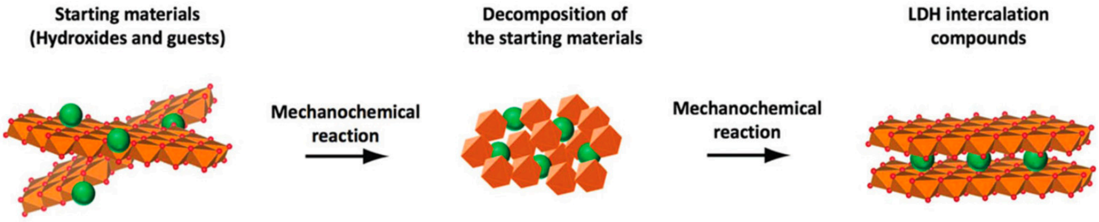

Figure 12. A schematic drawing of the formation of layered double hydroxides from raw materials by applying mechanochemical reaction. Reproduced with permission from reference [133].

A LiAl-OH LDH formed by grinding a mixture of $LiOH{\cdot}H_2O$ and $Al(OH)_3$ for 2–3 days followed by purging the mixture with the water saturated with N_2 gas at room temperature [134]. The formation of LDH occurred from the imbibition of LiOH and H_2O into $Al(OH)_3$ particles during mechanical mixing. It was reported that water was important to promote interparticle diffusion. Without purging water, the formation of LDHs did not occur. MgAl-NO_3 LDH was prepared by manual grinding the starting materials at room temperature [135]. Hydrate metal salts including $Mg(NO_3)_2$ and $Al(NO_3)_3$ were used instead of insoluble metal hydroxide precursors. Into the reaction, NaOH pellet was added as the hydroxide source. Nitrate intercalated LDH was obtained because of the rapid reaction of precursor which could prevent $CO_3{}^{2-}$ contamination. SEM observation exhibited the agglomerated plate-like LDH. The use of hydrated metal salts with atmospheric water (without the addition of water) was reported as an alternative procedure to synthesize LDH by mechanochemical method.

Two grinding steps including dry grinding followed by wet grinding (with the addition of water) have been used for the synthesis of LDHs. CaSn LDH where Sn^{4+} was incorporated into the hydroxide layers, which could not be achieved from conventional co-precipitation method, was reported to be successful by applying mechanochemically two-step grinding approach [136]. For the procedure, $CaCl_2$ and $SnCl_2$ as metal precursors were first dry ground using mortar and pestle for 1 h followed by the addition of 0.35 mL water to the mixture (0.35 mL H_2O to 3 g powder) and further ground until a uniform and homogeneous mixture was obtained. One step dry grinding the metal precursors for 3 h was done as comparison. It was shown that CaSn-LDH was not synthesized by using the co-precipitation method. Similarly, one step dry grinding did not produce a LDH because the water introduced with the precursor could not generate sufficient amounts of hydroxide group for the LDH structure. Whereas, two step dry and wet grinding was effective to obtain CaSn-LDH as shown by the XRD pattern, where three reflections ((003), (006), and (009)) due to LDH were seen. The aggregated lamellar was obtained assuming that the small particles stuck together to form larger aggregate in the size of several micrometers. One-pot synthesis of organic molecules containing LDH was done by mechanical grinding with the addition of a small amount of solvent [137]. Hexagonal platy particles with the size of 2 to 10 µm were obtained.

Post synthetic treatment was conducted to improve the crystallinity of LDH prepared from mechanochemical reaction. MgFe-CO_3 LDH and ZnAl-CO_3 LDH were prepared by two step grinding process at room temperature. The products were then peptized in a mixed ethanol and water solution [138]. From TEM images, particles showed the change from aggregated irregularly shaped particles to more regular, uniform, and monodispersed particles. They claimed that ethanol acted as stabilizing agent to protect the aggregation of particles from the interaction between hydroxyl group of ethanol with the surface of LDHs. Hydrothermal treatment was also applied to tailor the particle size and morphology of LDHs after mechanochemical grinding. Several LDHs ($M^{2+} = Mg^{2+}, Ni^{2+}, Zn^{2+}$ and $M^{3+} = Al^{3+}, Fe^{3+}$) were prepared by manual grinding the starting metal nitrate salts ($M^{2+}(NO_3)_2{\cdot}mH_2O$ and $M^{3+}(NO_3)_3{\cdot}nH_2O$) with NaOH and Na_2CO_3 at room temperature and then subjected to treat under hydrothermal condition at 100 °C for 24 h [139]. Comparing between hydrothermal treated and untreated one, the hydrothermal treated sample showed sharper intensity in the XRD patterns (Figure 13). The morphology of LDHs changed from irregular ultrafine nanoparticles to hexagonal shape for MgAl-LDH with an average diameter of 120 nm. It was proved that hydrothermal treatment could greatly improve the crystallinity and morphology of LDHs.

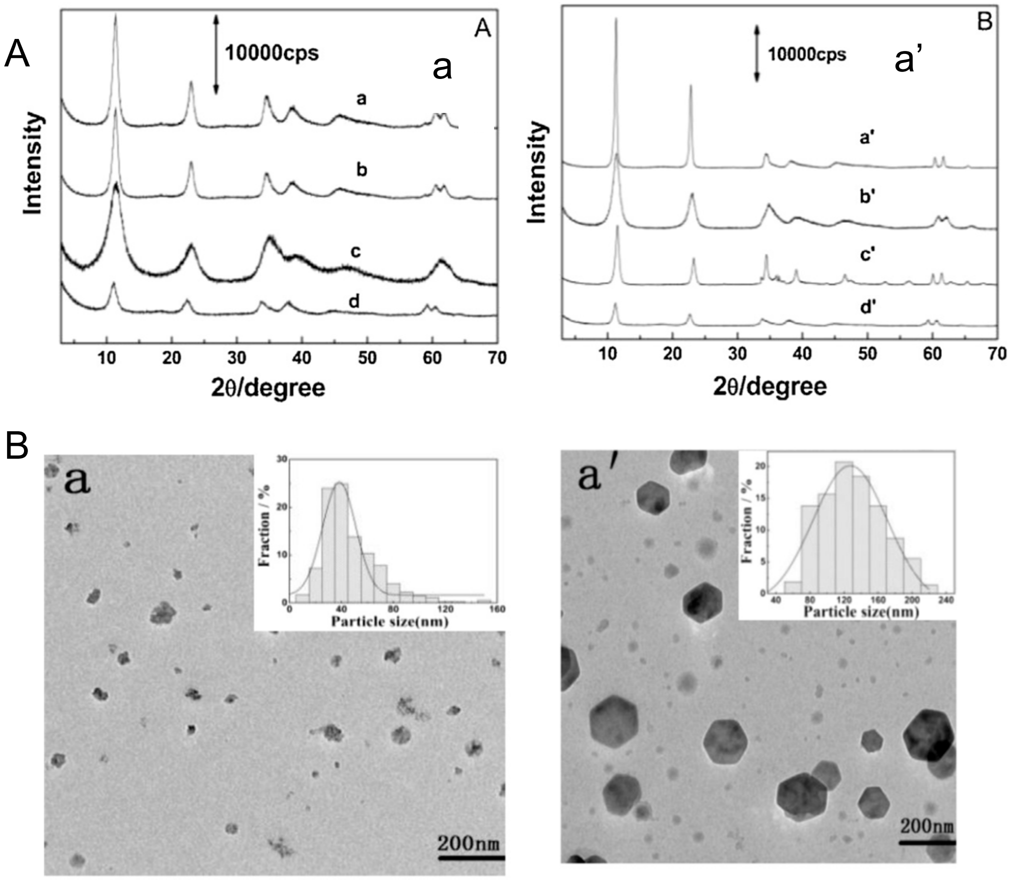

Figure 13. The variation of XRD pattern (**A**) and the TEM images (**B**) without hydrothermal treatment (a) and with hydrothermal treatment (a'). Reproduced with permission from reference [139].

Preparation of LDHs by using high energy mills has been reported. The preparation of Cl^-, NO_3^-, and SO_4^{2-} intercalated MgAl-LDH was done by using planetary ball mills to mix $Mg(OH)_2$ and aluminum salts ($AlCl_3$, $Al(NO_3)_3$ and $Al_2(SO_4)_3$) for 3–15 min followed by washing the product with DI water [140]. Though the formation of LDH with the targeted interlayer anion was confirmed, the Mg:Al ratio of the product was found to be smaller than the initial ratio of precursors. The importance of the precursor composition for the formation of LDH by mechanochemical milling was studied [141]. $Mg(OH)_2$ and $Al(OH)_3$ (at Mg:Al = 3–6) were mixed in a planetary ball mill for 15 min at room temperature to give MgAl-LDH (Mg:Al ratio = 3) and a part of $Mg(OH)_2$ was unreacted when the initial Mg:Al ratios were 4 and 6. The critical role of washing with water on the formation of the LDH was shown from the fact that the no reflection was seen in the XRD pattern of the product before the washing.

It is known that water is necessary to prepare LDHs for mechanochemical reaction. In order to promote the formation, two step operation including dry and wet milling was developed [142]. Mechanochemical syntheses of LDHs from $Mg(OH)_2$, $Al(OH)_3$, and $Mg(NO_3)_2$ were reported [142,143]. $Mg(OH)_2$ and $Al(OH)_3$ were mixed by using planetary ball mill for 1 h, then, $Mg(NO_3)_2{\cdot}6H_2O$ was added at the second step. As a reference, they prepared one-step milling by mixing all the starting materials from the beginning. The XRD, FTIR, and TG-DTA showed that, for the products prepared by one step milling, the remaining starting hydroxide was observed. It was speculated that wet milling reduced the efficiency of mechanochemical reaction, whereas two step milling exhibited the successful formation of the NO_3 intercalated LDH. From the results, they proposed the mechanism that, the first step dry milling led the starting metal hydroxide to be amorphous phase; then, by adding water in the second step (wet milling), the slurry led to the formation of LDHs [142]. Ni doped MgAl-LDH was also successfully prepared by applying two step milling operation [143].

The solid-state formation of organic anion intercalated LDHs has been reported [144,145]. MgAl-LDH intercalated with *p*-toluenesulfonate (TS-LDH), malonate (M-LDH), and oxalate anions (O-LDH) were synthesized by milling $Mg(OH)_2$ and $Al(OH)_3$ in the planetary ball mill for 1 h and subsequent milling with organic anions for another 1 h. The XRD patterns showed the diffraction patterns pointed to LDH materials with a *d* value of 1.77, 0.88, and 0.86 nm for TS-LDH, M-LDH, and O-LDH, respectively, indicating the successful synthesis of materials. The aggregated particles with a size over 700 nm were observed from the TEM image, together with the small disk-like particles having a lateral size of ca. 150 nm, suggesting the aggregation of primary particles during the reaction. The TS-LDH was used as the starting material for the anion exchange reaction with the dodecyl sulfate anion (abbreviated as DS). The XRD patterns showed the increasing of the basal spacing from 1.77 nm to 3.09 nm, and FTIR results also confirmed the formation of DS-LDH with the absence of absorption bands due to carbonate anions which was the advantage of the synthesis approach [144].

MgAl-acetate LDH film was prepared by casting the suspension of MgAl-acetate LDH on the substrate [145]. MgAl-acetate LDH was synthesized by a mechanochemical reaction using $Mg(OH)_2$ and $Al(OH)_3$ as the starting materials. The metal hydroxide precursors were added and milled in the planetary ball mil for 1 h. After the magnesium acetate was added as the acetate source, the mixture was milled for another 1 h. The ratio of Mg:Al:acetate was 3:1:1. The XRD pattern was ascribed to the acetate intercalated LDH with the *d* value of 1.19 nm [146–148]. FTIR and TG-DTA confirmed the formation of LDH with acetate anion. The LDH was dispersed into DI water under N_2 atmosphere and casted to form homogeneous MgAl-acetate film as seen in SEM image (Figure 14). The thickness of the film was controlled by changing the concentration of LDH from 3–20 g/L to be 1–3 μm. This film was used for the anion exchange reaction with coumarine-3-carboxylate, which was achieved by soaking the film into an ethanol solution containing coumarine-3-carboxylate to obtain a film with keeping its homogeneity.

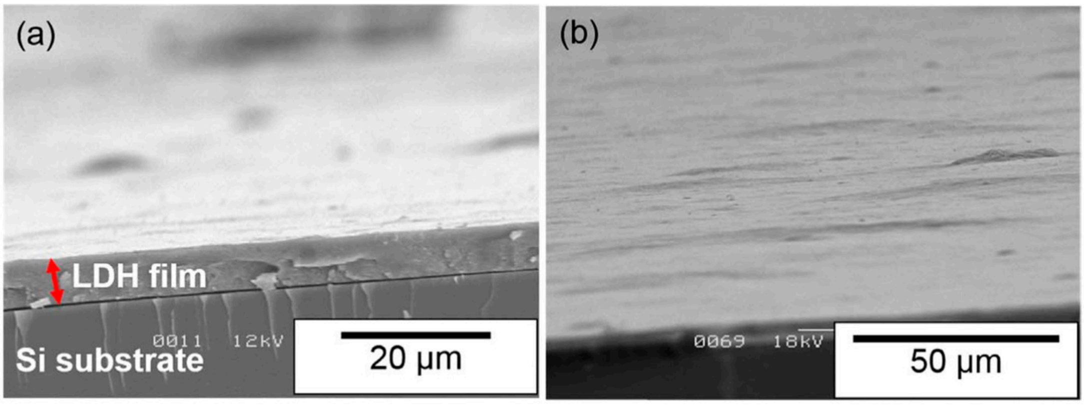

Figure 14. SEM image of the MgAl-acetate LDH film (**a**) at the edge and (**b**) on the surface. Reproduced with permission from reference [145].

Generally, two step milling operation led the thick-massive particles morphology. Second wet milling step was replaced by agitation to increase the crystallinity. The mixture of $Mg(OH)_2$ and $Al(OH)_3$ was milled for 1 h using planetary ball mill; then, the mixture was agitated in water for 1–5 h at room temperature [149]. The XRD result showed the increased crystallinity of LDH observed by the increasing of the sharpness of the diffraction peak when prolonging the agitation time. The importance of the combination of mechanochemical reaction and agitation step was investigated. $CuAl-CO_3$ LDH was prepared by milling $Cu_2(OH)_2CO_3$ and $Al(OH)_3$ in the planetary ball mill for 2 h, followed by agitating 1.0 g for the mixture in 100 mL DI water for 4 h [150]. Comparison with the one prepared by agitating the mixture in water without mechanochemical milling, the results showed that agitation without milling could not form LDH. They suggested that the amorphous state was necessary. The agitation caused the construction of LDH structure by adsorbing water to increase the crystallinity. ZnAl-CO_3 LDH was prepared by milling and subsequent agitation in water for 4 h [151]. The morphology was sheet-like particles which were different from thick-massive agglomerated particles prepared by the two-step milling operation. The author claimed that the agitation could prevent the impact of the particles and could prevent the limit of the particle growth caused in wet milling. Not only agitation but also ultrasonication have been used for the synthesis of various LDHs [152].

If compared with reported LDH syntheses using aqueous media, the solid-state synthesis of LDH has such advantages as (i) solid-liquid separation is not necessary, (ii) carbonate contamination is less plausible, and (iii) the starting materials are not expensive if compared with those used for the conventional syntheses starting from aqueous solution of metal salts. The variation of available LDHs and the morphology achieved by the mechanochemical method are still limited; therefore, the optimization of the synthesis condition is worth investigating further for a variety of LDHs.

5. Conclusions

The preparation of layered double hydroxides was summarized with the emphasis on the chemistry in the formation of layered double hydroxides. Due to the wide range of application, layered double hydroxides with various particle sizes and compositions are required. Efforts have been made to find the conditions for the synthesis of a variety of layered double hydroxides with controlled particle size from nm to micrometer. Further systematic studies on the preparation of layered double hydroxides will be done to obtain wider particle size variation and narrower particle size distribution as well as to find new functions based on the controlled composition. The bulk syntheses are an issue to be tackled for practical application.

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References

1. He, J.; Wei, M.; Li, B.; Kang, Y.; Evans, D.G.; Duan, X. Preparation of layered double hydroxides. *Struct. Bond.* **2006**, *119*, 89–119.
2. Evans, D.G.; Slade, R.C.T. Structural aspects of layered double hydroxides. *Struct. Bond.* **2006**, *119*, 1–87.
3. Rives, V. *Layered Double Hydroxides: Present and Future*; Nova Science Publishers Inc.: New York, NY, USA, 2001.
4. Cavani, F.; Trifiró, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today* **1991**, *11*, 173–301. [CrossRef]
5. Newman, S.P.; Jones, W. Synthesis, characterization and applications of layered double hydroxides containing organic guests. *New J. Chem.* **1998**, *22*, 105–115. [CrossRef]
6. Kuang, Y.; Zhao, L.; Zhang, S.; Zhang, F.; Dong, M.; Xu, S. Morphologies, preparations and applications of layered double hydroxide micro-/nanostructures. *Materials* **2010**, *3*, 5220–5235. [CrossRef]
7. Nishimura, S.; Takagaki, A.; Ebitani, K. Characterization, synthesis and catalysis of hydrotalcite-related materials for highly efficient materials transformations. *Green Chem.* **2013**, *15*, 2026–2042. [CrossRef]
8. Theiss, F.L.; Ayoko, G.A.; Frost, R.L. Synthesis of layered double hydroxides containing Mg^{2+}, Zn^{2+}, Ca^{2+} and Al^{3+} layer cations by co-precipitation methods—A review. *Appl. Surf. Sci.* **2016**, *383*, 200–213. [CrossRef]

9. Conterosito, E.; Gianotti, V.; Palin, L.; Boccaleri, E.; Viterbo, D.; Milanesio, M. Facile preparation methods of hydrotalcite layered materials and their structural characterization by combined techniques. *Inorg. Chim. Acta.* **2018**, *470*, 36–50. [CrossRef]
10. Sels, B.; Vos, D.D.; Buntinx, M.; Pierard, F.; Mesmaeker, A.K.; Jacobs, P. Layered double hydroxides exchanged with tungstate as biomimetic catalysts for mild oxidative bromination. *Nature* **1999**, *400*, 855–857. [CrossRef]
11. Choundary, B.M.; Madhi, S.N.; Chowdari, M.; Kantam, M.L.; Sreedhar, B. Layered double hydroxide supported nanopalladium catalyst for Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes. *J. Am. Chem. Soc.* **2002**, *124*, 14127–14136. [CrossRef]
12. Prevot, V.; Casal, B.; Ruiz-Hitzky, E. Intracrystalline alkylation of benzoate ions into layered double hydroxides. *J. Mater. Chem.* **2001**, *11*, 554–560. [CrossRef]
13. Yu, J.J.; Wang, X.P.; Li, L.D.; Hao, Z.P.; Xu, Z.P.; Lu, G.Q. Novel multi-functional mixed-oxide catalysts for effective NOx capture, decomposition, and reduction. *Adv. Func. Mater.* **2007**, *17*, 3598–3606. [CrossRef]
14. Kaneda, K.; Yamashita, T.; Matsushita, T.; Ebitani, K. Heterogeneous oxidation of allylic and benzylic alcohols catalyzed by Ru-Al-Mg hydrotalcites in the presence of molecular oxygen. *J. Org. Chem.* **1998**, *63*, 1750–1751. [CrossRef]
15. Costantino, U.; Leroux, F.; Nocchetti, M.; Mousty, C. LDH in physical, chemical, biochemical, and life sciences. *Devel. Clay Sci.* **2013**, *5*, 765–791.
16. Fan, G.; Li, F.; Evans, D.G.; Duan, X. Catalytic applications of layered double hydroxides: Recent advances and perspectives. *Chem. Soc. Rev.* **2014**, *43*, 7040–7066. [CrossRef] [PubMed]
17. Li, M.; Cheng, J.P.; Fang, J.H.; Yang, Y.; Liu, F.; Zhang, X.B. NiAl-layered double hydroxide/reduced graphene oxide composite: Microwave-assisted synthesis and supercapacitive properties. *Electrochim. Acta* **2014**, *134*, 309–318. [CrossRef]
18. Li, F.; Duan, X. Applications of layered double hydroxides. *Struct. Bond.* **2006**, *119*, 193–223.
19. Hoyo, D.C. Layered double hydroxides and human health: An overview. *Appl. Clay Sci.* **2007**, *36*, 103–121.
20. Zhao, M.; Zhao, Q.; Li, B.; Xue, H.; Pang, H.; Chen, C. Recent progress in layered double hydroxide based materials for electrochemical capacitors: Design, synthesis and performance. *Nanoscale* **2017**, *9*, 15206–15225. [CrossRef]
21. Inomata, K.; Ogawa, M. Preparation and properties of Mg/Al layered double hydroxide oleate and stearate intercalation compounds. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 336–342. [CrossRef]
22. Goodman-Gilman, A.; Goodman, L.S.; Gilman, A. *The Pharmacological Basis of Therapeutics, VI*; MacMillan Publishing Co, Inc.: New York, NY, USA, 1980; p. 995.
23. Hashimoto, Y.; Shiozawa, H.; Kishimoto, H.; Setoguchi, Y. Drug Composition: PCT—The International Patent System. Patent Number 95,307,512, 1997.
24. Tomohisa, M.; Mitsuo, H. Enteric Granule-Containing Tablets. U.S. Patent No. 5,798,120, 25 August 1998.
25. Woo, J.S.; Yi, H.G. Antifungal Oral Composition Containing Itraconazole and Process for Preparing Same. U.S. Patent No. 6,039,981, 21 March 2000.
26. Ambrogi, V.; Fardella, G.; Grandolini, G.; Perioli, L. Intercalation compounds of hydrotalcite-like anionic clays with antiinflammatory agents—I. Intercalation and in vitro release of ibuprofen. *Int. J. Pharm.* **2001**, *220*, 23–32. [CrossRef]
27. Khan, A.I.; Lei, L.; Norquist, A.J.; O'Hare, D. Intercalation and controlled release of pharmaceutically active compounds from a layered double hydroxide. *Chem. Commun.* **2001**, *22*, 2342–2343. [CrossRef]
28. Choy, J.H.; Oh, J.M.; Park, M.; Sohn, K.M.; Kim, J.W. Inorganic–biomolecular hybrid nanomaterials as a genetic molecular code system. *Adv. Mater.* **2004**, *16*, 1181–1184. [CrossRef]
29. Oh, J.M.; Park, M.; Kim, S.T.; Jung, J.Y.; Kang, Y.G.; Chong, J.H. Efficient delivery of anticancer drug MTX through MTX- LDH nanohybrid system. *J. Phys. Chem. Solids* **2006**, *67*, 1024–1027. [CrossRef]
30. Rojas, R.; Palena, M.C.; Jimenez-Kairuz, A.F.; Manzo, R.H.; Giacomelli, C.E. Modeling drug release from a layered double hydroxide–ibuprofen complex. *Appl. Clay Sci.* **2012**, *62–63*, 15–20. [CrossRef]
31. Choy, J.H.; Kwak, S.Y.; Park, S.J.; Jeong, Y.J.; Portier, J. Intercalative nanohybrids of nucleoside monophosphates and DNA in layered metal hydroxide. *J. Am. Chem. Soc.* **1999**, *121*, 1399–1400. [CrossRef]
32. Choy, J.H.; Kwak, S.Y.; Park, S.J.; Jeong, Y.J.; Portier, J. Inorganic layered double hydroxides as nonviral vectors. *Angew. Chem. Int. Ed.* **2000**, *39*, 4042–4045. [CrossRef]

33. Del Arco, M.; Cebadera, E.; Gutierrez, S.C.; Martin, M.; Montero, J.; Rives, V.; Rocha, J.; Sevilla, M.A. Mg,Al layered double hydroxides with intercalated indomethacin: Synthesis, characterization, and pharmacological study. *J. Pharm. Sci.* **2004**, *93*, 1649–1658. [CrossRef]
34. Nakayama, H.; Wada, N.; Tsuhako, M. Intercalation of amino acids and peptides into Mg-Al layered double hydroxide by reconstruction method. *Int. J. Pharm.* **2004**, *269*, 469–478. [CrossRef]
35. Aisawa, S.; Kudo, H.; Hoshi, T.; Takahashi, S.; Hirahara, H.; Umetsu, Y.; Narita, E. Intercalation behavior of amino acids into Zn-Al-layered double hydroxide by calcination-rehydration reaction. *J. Solid State Chem.* **2004**, *177*, 3987–3994. [CrossRef]
36. Choi, S.J.; Oh, J.M.; Choy, J.H. Anticancer drug-layered hydroxide nanohybrids as potent cancer chemotherapy agents. *J. Phys. Chem. Solids* **2008**, *69*, 1528–1532. [CrossRef]
37. Oh, J.M.; Choi, S.J.; Lee, G.E.; Kim, J.E.; Choy, J.H. Inorganic metal hydroxide nanoparticles for targeted cellular uptake through clathrin-mediated endocytosis. *Chem. Asian J.* **2009**, *4*, 67–73. [CrossRef]
38. Moujahid, E.M.; Besse, J.P.; Leroux, F. Poly(styrenesulfonate) layered double hydroxide nanocomposites. Stability and subsequent structural transformation with changes in temperature. *J. Mater. Chem.* **2003**, *13*, 258–264. [CrossRef]
39. Kottegoda, N.S.; Jones, W. Preparation and characterisation of Li-Al-glycine layered double hydroxides (LDHs)-polymer nanocomposites. *Macromol. Symp.* **2005**, *222*, 65–71. [CrossRef]
40. Lee, W.F.; Chen, Y.C. Superabsorbent polymeric materials. XIV. Preparation and water absorbency of nanocomposite superabsorbents containing intercalated hydrotalcite. *J. Appl. Polym. Sci.* **2004**, *94*, 2417–2424. [CrossRef]
41. Shichi, T.; Minamikawa, Y.; Yasuda, N.; Yamada, N.; Okamoto, Y.; Takagi, K. Enantioselective photopinacolization of benzophenone and benzhydrol intercalated in Mg-Al LDH interlayers. *Chem. Lett.* **2003**, *32*, 240–241. [CrossRef]
42. Takagi, K.; Shichi, T.; Usami, H.; Sawaki, Y. Controlled photocycloaddition of unsaturated carboxylates intercalated in hydrotalcite clay interlayers. *J. Am. Chem. Soc.* **1993**, *115*, 4339–4344. [CrossRef]
43. Liu, J.; Li, Y.; Huang, X.; Li, G.; Li, Z. Layered double hydroxide nano- and microstructures grown directly on metal substrates and their calcined products for application as li-ion battery electrodes. *Adv. Funct. Mater.* **2008**, *18*, 1448–1458. [CrossRef]
44. Yao, K.; Taniguchi, M.; Nakata, M.; Takahashi, M.; Yamagishi, A. Electrochemical scanning tunneling microscopy observation of ordered surface layers on an anionic clay-modified electrode. *Langmuir* **1998**, *14*, 2890–2895. [CrossRef]
45. Morigi, M.; Scavetta, E.; Berrettoni, M.; Giorgetti, M.; Tonelli, D. Sulfate-selective electrodes based on hydrotalcites. *Anal. Chim. Acta.* **2011**, *439*, 265–272. [CrossRef]
46. Scavetta, E.; Mignani, A.; Prandstraller, D.; Tonelli, D. Electrosynthesis of thin films of Ni, Al hydrotalcite like compounds. *Chem. Mater.* **2007**, *19*, 4523–4529. [CrossRef]
47. Trifiro, F.; Vaccari, A. *Handbook of Layered Materials*; Marcel Dekker: New York, NY, USA, 2004; p. 251.
48. Reichle, W.T. Synthesis of anionic clay-minerals (mixed metal-hydroxides, hydrotalcite). *Solid States Ionics* **1986**, *22*, 135–141. [CrossRef]
49. Intasa-Ard, G.S.; Bureekaew, S.; Ogawa, M. Efficient production of MgAl layered double hydroxide nanoparticle. *J. Ceram. Soc. Jpn.* **2019**, *127*, 11–17. [CrossRef]
50. Yun, S.K.; Pinnavaia, T.J. Water content and particle texture of synthetic hydrotalcite-like layered double hydroxides. *Chem. Mater.* **1995**, *7*, 348–354. [CrossRef]
51. Aisawa, S.; Takahashi, S.; Ogasawara, W.; Umetsu, Y.; Narita, E. Direct intercalation of amino acids into layered double hydroxides by coprecipitation. *J. Solid State Chem.* **2001**, *162*, 52–62. [CrossRef]
52. Li, Y.; Gao, B.; Wu, T.; Sun, D.; Li, X.; Wang, B.; Lu, F. Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide. *Water Res.* **2009**, *43*, 3067–3075. [CrossRef]
53. Zhang, H.; Zou, K.; Guo, S.; Duan, X. Nanostructural drug-inorganic clay composites: Structure, thermal property and in vitro release of captopril-intercalated Mg–Al-layered double hydroxides. *J. Solid State Chem.* **2006**, *179*, 1792–1801. [CrossRef]
54. Zhang, H.; Pan, D.; Zou, K.; He, J.; Duan, X. A novel core-shell structured magnetic organic-inorganic nanohybrid involving drug-intercalated layered double hydroxides coated on a magnesium ferrite core for magnetically controlled drug release. *J. Mater. Chem.* **2009**, *19*, 3069–3077. [CrossRef]

55. Choi, S.J.; Oh, J.M.; Choy, J.H. Safety aspect of inorganic layered nanoparticles: Size-dependency in vitro and in vivo. *J. Nanosci. Nanotechnol.* **2008**, *8*, 5297–5301. [CrossRef]
56. Chakraborty, M.; Dasgupta, S.; Sengupta, S.; Chakraborty, J.; Ghosh, S.; Ghosh, J.; Basu, D. A facile synthetic strategy for Mg–Al layered double hydroxide material as nanocarrier for methotrexate. *Ceram. Int.* **2012**, *38*, 941–949. [CrossRef]
57. Huang, W.; Zhang, H.; Pan, D. Study on the release behavior and mechanism by monitoring the morphology changes of the large-sized drug-LDH nanohybrids. *AIChE J.* **2011**, *57*, 1936–1946. [CrossRef]
58. Parida, K.M.; Mohapatra, L. Carbonate intercalated Zn/Fe layered double hydroxide: A novel photocatalyst for the enhanced photo degradation of azo dyes. *Chem. Eng. J.* **2012**, *179*, 131–139. [CrossRef]
59. Cantrell, D.G.; Gillie, L.J.; Lee, A.F.; Wilson, K. Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. *Appl. Catal. A-GEN* **2005**, *287*, 183–190. [CrossRef]
60. Darder, M.; López-Blanco, M.; Aranda, P.; Leroux, F.; Ruiz-Hitzky, E. Bio-nanocomposites based on layered double hydroxides. *Chem. Mater.* **2005**, *17*, 1969–1977. [CrossRef]
61. Oh, J.M.; Hwang, S.H.; Choy, J.H. The effect of synthetic conditions on tailoring the size of hydrotalcite particles. *Solid State Ionics* **2002**, *151*, 285–291. [CrossRef]
62. Carja, G.; Nakamura, R.; Aida, T.; Niiyama, H. Textural properties of layered double hydroxides: Effect of magnesium substitution by copper or iron. *Microporous Mesoporous Mater.* **2001**, *47*, 275–284. [CrossRef]
63. Shan, R.R.; Yan, L.G.; Yang, Y.M.; Yang, K.; Yu, S.J.; Yu, H.Q.; Du, B. Highly efficient removal of three red dyes by adsorption onto Mg–Al-layered double hydroxide. *J. Ind. Eng. Chem.* **2015**, *21*, 561–568. [CrossRef]
64. Leroux, F.; Gachon, J.; Besse, J.P. Biopolymer immobilization during the crystalline growth of layered double hydroxide. *J. Solid State Chem.* **2004**, *177*, 245–250. [CrossRef]
65. Gao, P.; Li, F.; Zhan, H.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y. Influence of Zr on the performance of Cu/Zn/Al/Zr catalysts via hydrotalcite-like precursors for CO_2 hydrogenation to methanol. *J. Catal.* **2013**, *298*, 51–60. [CrossRef]
66. Cao, F.; Wang, Y.; Ping, Q.; Liao, Z. Zn–Al–NO_3-layered double hydroxides with intercalated diclofenac for ocular delivery. *Int. J. Pharm.* **2011**, *404*, 250–256. [CrossRef]
67. Xu, Z.P.; Stevenson, G.; Lu, C.Q.; Lu, G.Q. Dispersion and size control of layered double hydroxide nanoparticles in aqueous solutions. *J. Phys. Chem. B.* **2006**, *110*, 16923–16929. [CrossRef]
68. Choy, J.H.; Kwak, S.Y.; Park, J.S.; Jeong, Y.J. Cellular uptake behavior of [γ-32P] labeled ATP–LDH nanohybrids. *J. Mater. Chem.* **2001**, *11*, 1671–1674. [CrossRef]
69. Gu, Z.; Thomas, A.C.; Xu, Z.P.; Campbell, J.H.; Lu, G.Q. In vitro sustained release of LMWH from MgAl-layered double hydroxide nanohybrids. *Chem. Mater.* **2008**, *20*, 3715–3722. [CrossRef]
70. Ulibarri, M.A.; Pavlovic, I.; Barriga, C.; Hermosın, M.C.; Cornejo, J. Adsorption of anionic species on hydrotalcite-like compounds: Effect of interlayer anion and crystallinity. *Appl. Clay Sci.* **2001**, *18*, 17–27. [CrossRef]
71. Kloprogge, J.T.; Hickey, L.; Frost, R.L. The effects of synthesis pH and hydrothermal treatment on the formation of zinc aluminum hydrotalcites. *J. Solid State Chem.* **2004**, *177*, 4047–4057. [CrossRef]
72. Pan, D.; Zhang, H.; Fan, T.; Chen, J.; Duan, X. Nearly monodispersed core–shell structural Fe_3O_4@DFUR–LDH submicro particles for magnetically controlled drug delivery and release. *Chem. Commun.* **2011**, *47*, 908–910. [CrossRef]
73. Raki, L.; Beaudoin, J.J.; Mitchell, L. Layered double hydroxide-like materials: Nanocomposites for use in concrete. *Cement Concrete Res.* **2004**, *34*, 1717–1724. [CrossRef]
74. Li, Y.W.; Yao, J.H.; Liu, C.J.; Zhao, W.M.; Deng, W.X.; Zhong, S.K. Effect of interlayer anions on the electrochemical performance of Al-substituted α-type nickel hydroxide electrodes. *Int. J. Hydrog. Energy* **2010**, *35*, 2539–2545. [CrossRef]
75. Géraud, E.; Rafqah, S.; Sarakha, M.; Forano, C.; Prevot, V.; Leroux, F. Three dimensionally ordered macroporous layered double hydroxides: Preparation by templated impregnation/coprecipitation and pattern stability upon calcination. *Chem. Mater.* **2007**, *20*, 1116–1125. [CrossRef]
76. Li, B.; He, J.; Evans, D.G.; Duan, X. Inorganic layered double hydroxides as a drug delivery system—Intercalation and in vitro release of fenbufen. *Appl. Clay Sci.* **2004**, *27*, 199–207. [CrossRef]
77. Kang, D.; Yu, X.; Tong, S.; Ge, M.; Zuo, J.; Cao, C.; Song, W. Performance and mechanism of Mg/Fe layered double hydroxides for fluoride and arsenate removal from aqueous solution. *Chem. Eng. J.* **2013**, *228*, 731–740. [CrossRef]

78. Nitoh, K.; Ayral, A.; Ogawa, M. Preparation of well-defined nanometer-sized layered double hydroxides by novel pH adjustment method using ion-exchange resin. *Chem. Lett.* **2010**, *39*, 1018–1019. [CrossRef]
79. Naito, S.; Nitoh, K.; Ayral, A.; Ogawa, M. Preparation of finite particles of nitrate forms of layered double hydroxides by pH adjustment with anion exchange resin. *Ind. Eng. Chem. Res.* **2012**, *51*, 14414–14418. [CrossRef]
80. Li, K.; Kumada, N.; Yonesaki, Y.; Takei, T.; Kinomura, N.; Wang, H.; Wang, C. The pH effects on the formation of Ni/Al nitrate form layered double hydroxides (LDHs) by chemical precipitation and hydrothermal method. *Mater. Chem. Phys.* **2010**, *121*, 223–229. [CrossRef]
81. Ogawa, M.; Inomata, K. Preparation of layered double hydroxides. *Clay Sci.* **2011**, *15*, 131–137.
82. Reichle, W.T. Catalytic reactions by thermally activated, synthetic, anionic clay minerals. *J. Catal.* **1985**, *94*, 547–557. [CrossRef]
83. Miyata, S. The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties-I: The Systems Mg^{2+}-Al^{3+}-NO_3^-, Mg^{2+}-Al^{3+}-Cl^-, Mg^{2+}-Al $^{3+}$-ClO_4^-, Ni^{2+}-Al^{3+}-Cl^- and Zn^{2+}-Al^{3+}-Cl^-. *Clays Clay Miner.* **1975**, *23*, 369–375. [CrossRef]
84. Miyata, S.; Akira, O. Synthesis of hydrotalcite-like compounds and their physico-chemical properties-the systems Mg^{2+}-Al^{3+}-SO_4^{2-} and Mg^{2+}-Al^{3+}-CrO_4^{2-}. *Clays Clay Miner.* **1977**, *25*, 14–18. [CrossRef]
85. Miyata, S. Physico-chemical properties of synthetic hydrotalcites in relation to composition. *Clays Clay miner.* **1980**, *28*, 50–56. [CrossRef]
86. Zhao, S.; Yi, H.; Tang, X.; Gao, F.; Yu, Q.; Zhou, Y.; Yang, Z. Enhancement effects of ultrasound assisted in the synthesis of NiAl hydrotalcite for carbonyl sulfide removal. *Ultrason. Sonochem.* **2016**, *32*, 336–342. [CrossRef]
87. Climent, J.M.; Corma, A.; Iborra, S.; Epping, K.; Velty, A. Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures. *J. Catal.* **2004**, *225*, 316–326. [CrossRef]
88. Zhao, Y.; Li, F.; Zhang, R.; Evans, D.G.; Duan, X. Preparation of layered double-hydroxide nanomaterials with a uniform crystallite size using a new method involving separate nucleation and aging steps. *Chem. Mater.* **2002**, *14*, 4286–4291. [CrossRef]
89. Feng, Y.; Li, D.; Li, C.; Wang, Z.; Evans, D.G.; Duan, X. Synthesis of Cu-containing layered double hydroxides with a narrow crystallite-size distribution. *Clays Clay Miner.* **2003**, *51*, 566–569. [CrossRef]
90. Chang, Z.; Evans, D.G.; Duan, X.; Vial, C.; Ghanbaja, J.; Prevot, V.; Forano, C. Synthesis of [Zn–Al–CO_3] layered double hydroxides by a coprecipitation method under steady-state conditions. *J. Solid State Chem.* **2005**, *178*, 2766–2777. [CrossRef]
91. Shiba, K.; Ogawa, M. Precise Synthesis of well-defined inorganic-organic hybrid particles. *Chem. Rec.* **2018**, *18*, 950–968. [CrossRef]
92. Pang, X.; Sun, M.; Ma, X.; Hou, W. Synthesis of layered double hydroxide nanosheets by coprecipitation using a T-type microchannel reactor. *J. Solid State Chem.* **2014**, *210*, 111–115. [CrossRef]
93. Labajos, F.M.; Rives, V.; Ulibarri, M.A. Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite-like materials. *J. Mater. Sci.* **1992**, *27*, 1546–1552. [CrossRef]
94. Benito, P.; Guinea, I.; Herrero, M.; Labajos, M.F.; Rives, V. Incidence of microwave hydrothermal treatments on the crystallinity properties of hydrotalcite-like compounds. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1815–1819. [CrossRef]
95. Benito, P.; Labajos, F.M.; Rives, V. Microwaves and layered double hydroxides: A smooth understanding. *Pure Appl. Chem.* **2009**, *81*, 1459–1471. [CrossRef]
96. Sugimoto, T. *Monodispersed Particles*; Elsevier: Amsterdam, The Netherlands, 2001.
97. Costantino, U.; Marmottini, F.; Nocchetti, M.; Vivan, R. New synthetic routes to hydrotalcite-like compounds–Characterization and properties of the obtained materials. *Eur. J. Inorg. Chem.* **1998**, *10*, 1439–1446. [CrossRef]
98. Inayat, A.; Klumpp, M.; Schwieger, W. The urea method for the direct synthesis of ZnAl layered double hydroxides with nitrate as the interlayer anion. *Appl. Clay Sci.* **2011**, *51*, 452–459. [CrossRef]
99. Staal, L.B.; Pushparaj, S.S.C.; Forano, C.; Prevot, V.; Ravnsbæk, D.B.; Bjerring, M.; Nielsen, U.G. Competitive reactions during synthesis of zinc aluminum layered double hydroxides by thermal hydrolysis of urea. *J. Mater. Chem. A* **2017**, *5*, 21795–21806. [CrossRef]
100. Narita, E.; Takahashi, Y.; Umetsu, Y. Synthesis of highly crystalline Al-Li layered double hydroxide by homogeneous precipitation method. *Nippon Kagaku Kaishi* **2001**, *5*, 273–279. [CrossRef]

101. Liu, Z.; Ma, R.; Osada, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. Synthesis, anion exchange, and delamination of Co-Al layered double hydroxide: Assembly of the exfoliated nanosheet/polyanion composite films and magneto-optical studies. *J. Am. Chem. Soc.* **2006**, *128*, 4872–4880. [CrossRef]
102. Adachi-Pagano, M.; Forano, C.; Besse, J.-P. Synthesis of Al-rich hydrotalcite-like compounds by using the urea hydrolysis reaction-control of size and morphology. *J. Mater. Chem.* **2003**, *13*, 1988–1993. [CrossRef]
103. Iyi, N.; Tamura, K.; Yamada, H. One-pot synthesis of organophilic layered double hydroxides (LDHs) containing aliphatic carboxylates: Extended "homogeneous precipitation" method. *J. Colloid Interface Sci.* **2009**, *340*, 67–73. [CrossRef]
104. Perioli, L.; Ambrogi, V.; Rossi, C.; Latterini, L.; Nocchetti, M.; Costantino, U. Use of anionic clays for photoprotection and sunscreen photostability: Hydrotalcites and phenylbenzimidazole sulfonic acid. *J. Phys. Chem. Solids* **2006**, *67*, 1079–1083. [CrossRef]
105. Iyi, N.; Matsumoto, T.; Kaneko, Y.; Kitamura, K. A novel synthetic route to layered double hydroxides using hexamethylenetetramine. *Chem. Lett.* **2004**, *33*, 1122–1123. [CrossRef]
106. Ogawa, M.; Kaiho, H. Homogeneous precipitation of uniform hydrotalcite particles. *Langmuir* **2002**, *18*, 4240–4242. [CrossRef]
107. Kayano, M.; Ogawa, M. Preparation of large platy particles of Co-Al layered double hydroxides. *Clays Clay Miner.* **2006**, *54*, 385–392. [CrossRef]
108. Kayano, M.; Ogawa, M. Controlled particle size and size distribution of Co-Al layered double hydroxide via the hydrothermal urea method in aqueous alcohols. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1988–1990. [CrossRef]
109. Arai, Y.; Ogawa, M. Preparation of Co-Al layered double hydroxides by the hydrothermal urea method for controlled particle size. *Appl. Clay Sci.* **2009**, *42*, 601–604. [CrossRef]
110. Pérez-Ramírez, J.; Mul, G.; Kapteijn, F.; Moulijn, J.A. In situ investigation of the thermal decomposition of Co–Al hydrotalcite in different atmospheres. *J. Mater. Chem.* **2001**, *11*, 821–830. [CrossRef]
111. Kloprogge, J.T.; Frost, R.L. Fourier transform and Raman spectroscopic study of the local structure of Mg-, Ni-, and Co-hydrotalcites. *J. Solid State Chem.* **1999**, *146*, 506–515. [CrossRef]
112. Shaw, W.H.R.; Bordeaux, J.J. The decomposition of urea in aqueous media. *J. Am. Chem. Soc.* **1955**, *77*, 4729–4733. [CrossRef]
113. He, J.; Li, B.; Evans, D.G.; Duan, X. Synthesis of layered double hydroxides in an emulsion solution. *Colloids Surf. A Physicochem. Eng. Aspects* **2004**, *251*, 191–196. [CrossRef]
114. Hu, G.; O'Hare, D. Unique layered double hydroxide morphologies using reverse microemulsion synthesis. *J. Am. Chem. Soc.* **2005**, *127*, 17808–17813. [CrossRef]
115. Hu, G.; Wang, N.; O'Hare, D.; Davis, J. Synthesis of magnesium aluminium layered double hydroxides in reverse microemulsions. *J. Mater. Chem.* **2007**, *17*, 2257–2266. [CrossRef]
116. Bellezza, F.; Cipiciani, A.; Costantino, U.; Nocchetti, N.; Posati, T. Hydrotalcite-Like Nanocrystals from Water-in-Oil Microemulsions. *Eur. J. Inorg. Chem.* **2009**, *18*, 2603–2611. [CrossRef]
117. Bellezza, F.; Nocchetti, M.; Posati, T.; Giovagnoli, S.; Cipiciani, A. Synthesis of colloidal dispersions of NiAl, ZnAl, NiCr, ZnCr, NiFe, and MgFe hydrotalcite-like nanoparticles. *J. Colloid Interface Sci.* **2012**, *376*, 20–27. [CrossRef]
118. Ogawa, M.; Asai, S. Hydrothermal synthesis of layered double hydroxide-deoxycholate intercalation compounds. *Chem. Mater.* **2000**, *12*, 3253–3255. [CrossRef]
119. Ogawa, M.; Saito, F. Easily oxidizable polysulfide anion occluded in the interlayer space of Mg/Al layered double hydroxide. *Chem. Lett.* **2004**, *33*, 1030–1031. [CrossRef]
120. Ogawa, M.; Sugiyama, Y. Facile synthesis of Zn-Al layered double hydroxide from aqueous suspension of zinc oxide and aluminum hydroxide. *J. Ceram. Soc. Jpn.* **2009**, *117*, 179–184. [CrossRef]
121. Newman, S.P.; Jones, W.; O'Corner, P.; Stamires, D.N. Synthesis of the $3R_2$ polytype of a hydrotalcite-like mineral. *J. Mater. Chem.* **2002**, *12*, 153–155. [CrossRef]
122. Xu, P.Z.; Lu, Q.G. Hydrothermal synthesis of Layered Double Hydroxides (LDHs) from mixed MgO and Al_2O_3: LDH formation mechanism. *Chem. Mater.* **2005**, *17*, 1055–1062. [CrossRef]
123. Mitchell, S.; Biswick, T.; Jones, W.; Williams, G.; O'Hare, D. A synchrotron radiation study of the hydrothermal synthesis of layered double hydroxides from MgO and Al_2O_3 slurries. *Green Chem.* **2007**, *9*, 373–378. [CrossRef]
124. Chitrakar, R.; Tezuka, S.; Sonoda, A.; Sakane, K.; Ooi, K.; Hirotsu, T. A solvent-free synthesis of Zn-Al layered double hydroxides. *Chem. Lett.* **2007**, *36*, 446–447. [CrossRef]

125. Senna, M. Chemical powder technology—A new insight into atomic processes on the surface of fine particles. *Adv. Powder. Tech.* **2002**, *3*, 115–138. [CrossRef]
126. Braga, D.; Giaffreda, S.L.; Grepioni, F.; Pettersen, A.; Maini, L.; Curzi, M.; Polito, M. Mechanochemical preparation of molecular and supramolecular organometallic materials and coordination networks. *Dalton trans.* **2006**, *10*, 1249–1263. [CrossRef]
127. Pichon, A.; Lazuen-Garay, A.; James, S.L. Solvent-free synthesis of a microporous metal–organic framework. *Cryst. Eng. Comm.* **2006**, *8*, 211–214. [CrossRef]
128. Baláž, P.; Achimovičová, M.; Baláž, M.; Billik, P.; Cherkezova-Zheleva, Z.; Criado, J.M.; Delogu, F.; Dutková, E.; Gaffet, E.; Gotor, F.J.; et al. Hallmarks of mechanochemistry: From nanoparticles to technology. *Chem. Soc. Rev.* **2013**, *42*, 7571–7637. [CrossRef]
129. Takacs, L. The historical development of mechanochemistry. *Chem. Soc. Rev.* **2013**, *42*, 7649–7659. [CrossRef]
130. Wang, G.W. Mechanochemical organic synthesis. *Chem. Soc. Rev.* **2013**, *42*, 7668–7700. [CrossRef]
131. Alex, T.C.; Kumar, R.; Roy, S.K.; Mehrotra, S.P. Mechanical activation of Al-oxyhydroxide minerals–a review. *Miner. Process. Extr. Metall. Rev.* **2016**, *37*, 1–26. [CrossRef]
132. Zhang, P.; Dai, S. Mechanochemical synthesis of porous organic materials. *J. Mater. Chem. A* **2017**, *5*, 16118–16127. [CrossRef]
133. Intasa-Ard, G.S.; Imwiset, J.K.; Bureekaew, S.; Ogawa, M. Mechanochemical methods for the preparation of intercalation compounds, from intercalation to the formation of layered double hydroxides. *Dalton Trans.* **2018**, *47*, 2896–2916. [CrossRef]
134. Poeppelmeier, K.R.; Hwu, S.J. Synthesis of lithium dialuminate by salt imbibition. *Inorg. Chem.* **1987**, *26*, 3297–3302. [CrossRef]
135. Ay, A.N.; Zümreoglu-Karan, B.; Mafra, L. A Simple Mechanochemical Route to Layered Double Hydroxides: Synthesis of Hydrotalcite-Like Mg-Al-NO_3-LDH by Manual Grinding in a Mortar. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1470–1475. [CrossRef]
136. Ferencz, Z.; Szabados, M.; Ádok-Sipiczki, M.; Kukovecz, Á.; Kónya, Z.; Sipos, P.; Pálinkó, I. Mechanochemically assisted synthesis of pristine Ca (II) Sn (IV)-layered double hydroxides and their amino acid intercalated nanocomposites. *J. Mater. Sci.* **2014**, *49*, 8478–8486. [CrossRef]
137. Conterosito, E.; Van Beek, W.; Palin, L.; Croce, G.; Perioli, L.; Viterbo, D.; Gatti, G.; Milanesio, M. Development of a fast and clean intercalation method for organic molecules into layered double hydroxides. *Cryst. Growth Des.* **2013**, *13*, 1162–1169. [CrossRef]
138. Jia, C.; Zhang, X.; Li, S. Studies on mechanochemical method to synthesize LDH nanoparticles. *Chin. J. Chem.* **2012**, *30*, 277–282. [CrossRef]
139. Zhang, X.; Li, S. Mechanochemical approach for synthesis of layered double hydroxides. *Appl. Surf. Sci.* **2013**, *274*, 158–163. [CrossRef]
140. Isupov, V.P.; Chupakhina, L.E.; Mitrofanova, R.P. Mechanochemical synthesis of double hydroxides. *J. Mater. Synth. Process.* **2000**, *8*, 251–253. [CrossRef]
141. Khusnutdinov, V.P.; Isupov, V.P. Mechanochemical synthesis of a hydroxycarbonate form of layered magnesium aluminum hydroxides. *Inorg. Mater.* **2008**, *44*, 263–267. [CrossRef]
142. Tongamp, W.; Zhang, Q.; Saito, F. Mechanochemical route for synthesizing nitrate form of layered double hydroxide. *Powder Technol.* **2008**, *185*, 43–48. [CrossRef]
143. Tongamp, W.; Zhang, Q.; Saito, F. Generation of hydrogen gas from polyethylene mechanically milled with Ni-doped layered double hydroxide. *Fuel Process. Technol.* **2009**, *90*, 909–913. [CrossRef]
144. Kuramoto, K.; Ogawa, M. Preparation of layered double hydroxide–organic intercalation compounds by solid–solid reactions. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 675–677. [CrossRef]
145. Kuramoto, K.; Intasa-Ard, G.S.; Bureekaew, S.; Ogawa, M. Mechanochemical synthesis of finite particle of layered double hydroxide-acetate intercalation compound: Swelling, thin film and ion exchange. *J. Solid State Chem.* **2017**, *253*, 147–151. [CrossRef]
146. Meyn, M.; Beneke, K.; Lagaly, G. Anion-exchange reactions of layered double hydroxides. *Inorg. Chem.* **1990**, *29*, 5201–5207. [CrossRef]
147. Kelkar, C.P.; Schutz, A.A. Ni-, Mg- and Co-containing hydrotalcite-like materials with a sheet-like morphology: Synthesis and characterization. *Microporous Mater.* **1997**, *10*, 163–172. [CrossRef]
148. Greenwell, H.C.; Jones, W.; Stamires, D.N.; O'Connor, P.; Brady, M.F. A one-pot synthesis of hybrid organo-layered double hydroxide catalyst precursors. *Green Chem.* **2006**, *8*, 1067–1072. [CrossRef]

149. Wang, B.; Qu, J.; Li, X.; He, X.; Zhang, Q. Precursor Preparation to Promote the Adsorption of Mg-Al Layered Double Hydroxide. *J. Am. Ceram. Soc.* **2016**, *99*, 2882–2885. [CrossRef]
150. Qu, J.; He, X.; Chen, M.; Hu, H.; Zhang, Q.; Liu, X. Mechanochemical synthesis of Cu-Al and methyl orange intercalated Cu-Al layered double hydroxides. *Mater. Chem. Phys.* **2017**, *191*, 173–180. [CrossRef]
151. Qu, J.; He, X.; Chen, M.; Huang, P.; Zhang, Q.; Liu, X. A facile mechanochemical approach to synthesize Zn-Al layered double hydroxide. *J. Solid State Chem.* **2017**, *250*, 1–5. [CrossRef]
152. Szabados, M.; Bús, C.; Adok-Sipiczki, M.; Kónya, Z.; Kukovecz, Á.; Sipos, P.; Pálinkó, I. Ultrasound-enhanced milling in the synthesis of phase-pure, highly crystalline ZnAl-layered double hydroxide of low Zn (II) content. *Particuology* **2016**, *27*, 29–33. [CrossRef]