Mechanochemical Synthesis of Layered Double Hydroxides

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Abstract. Hydrotalcite-like layered double hydroxide was successfully synthesised from metal oxides and hydroxides using a horizontal bead mill and was identified as a mixture of hydrotalcite and meixnerite. The final thermally aged material that was milled for three hours has a particle size distribution in the range 0.5µm to 12µm. XRD and FTIR both suggest that the synthesised material is phase-pure LDH but the amorphous halo present in the XRD results suggests that an amorphous compound is present as a contaminant.

INTRODUCTION

Layered double hydroxides (LDH) are a class of anionic clays with many uses and applications, they are made up of a series of layered mixed metal hydroxides and an interlayer of anions. LDH materials find use in industry as flame retardants, catalyst packing, reaction catalysts, medicine delivery systems, adsorbers of halogen free radicals, waste water purifiers and many other useful products. [2, 1021-1022]

LDHs are specifically useful as flame retardants, smoke suppresants, reinforcing fillers, and acid scavengers in polymer compounds. The LDHs are non-toxic and heavy metal free, green alternatives to many additives currently used in the polymer industry. The problem with LDH synthesis is that all of the possible synthesis techniques either involve large amounts of waste water and metal salt effluent or require large amounts of energy to occur when large scale industrial production is concerned [1]. To determine if the mechanochemical synthesis is a viable synthesis technique, the existing techniques for LDH synthesis need to be understood.

Co-precipitation Method

The first technique discussed is the co-precipitation method, where aqueous solutions of the metal salts used to synthesise the desired LDH are added together in specific ratios at high stirring speeds, constant temperatures and high pH values using an inorganic base such as NaOH. The precipitate must then be hydrothermally aged to increase the crystallinity of the mixture using the process of Ostwald ripening. Advantages of this technique include the production of small particles before aging with high crystallinity after aging. The disadvantage of this technique is the large volume production of salt containing effluent and the size trade-off experienced during aging. [2, 1027–1028]

Urea Method

The urea method is very similar to the co-precipitation method, with the only difference being the use of urea as the base instead of an inorganic chemical base such as NaOH. This reaction takes place more slowly and as such it can be controlled more accurately to produce more closely distributed particle sizes, and does not require as severe washing due to the lack of the base metal and salt contaminants. [2, 1028-1029]

Dissolution Precipitation Method

The next method discussed is the dissolution precipitation method - or two powder synthesis method - in which the metal oxides or hydroxides are used as the reagents for the LDH synthesis. Labuschagne, Giesekke, and Van Schalk-´wyk [3] used this method to develop a one-step synthesis process with zero effluent for the synthesis of hydrotalcite. The method suggests a temperature within the range from $140°C$ to $200°C$ is held for between 4 and 6 hours at a pressure between 10bar to 14bar in order to produce hydrotalcite. This is the first method with no effluent, but the reaction conditions suggest that the process would be energy intensive in order to keep the reaction vessel at that high temperature for a long period of time.

Mechanochemistry

There have been some promising results in literature showing that LDH materials can be created using mechanochemistry. Mechanochemistry is the use of mechanical energy to affect a chemical reaction [4] and includes using a multitude of mechanical processes such as crushing, grinding, thermal shock and many other machining techniques to affect polymorphic transformations, solid surface property activation, crystal structure alteration, and solid state reactions on varying types of materials from metals to pharmaceuticals [5]. For the purpose of this investigation, only the use of grinding or milling and thermal treatment are considered.

A patent assigned to Sud-Chemie [6] describes a method for the synthesis and manufacture of hydrotalcite¨ whereby one or both of the starting compounds are not used in the form of a solution. The mixture is subjected to intensive wet grinding, and further processing can lead to either a crystalline phase or an amorphous phase of a high quality hydrotalcite. The patent suggests starting compounds including unreactive MgO, $Al(OH)_3$ and CO_2 either in the form of carbonated water, gas or dry ice. It was found that where the hydrotalcite would be incorporated into a polymer, it is best if milling occurs until such a time that the material is milled down to a D_{90} cut size of 3µm. [6]

Isupov, Chupakhina, and Mitrofanova [7] used a high-energy planetary-type activator to perform mechanochemical synthesis of magnesium-aluminium double hydroxides starting with a mixture of magnesium hydroxide and aluminium salts [7], where the interlayer spacing and species were determined by the anion in the aluminium salt. Khusnutdinov and Isupov [8] used a planetary mill to create a phase-pure magnesium-aluminium LDH from magnesium hydroxide, aluminium hydroxide and sodium bicarbonate. The interlayer of the LDH consisted of both carbonate and bicarbonate ions. The mill type allowed for 40g samples to be synthesised at one time, and the milling was carried out for approximately 15 minutes before the samples were washed with water.

Ferencz *et al.* [9] used a two step mechanochemical process with a minute and controlled amount of water to produce almost phase pure Ca-Al LDH. The mill used for the synthesis was a mixer mill using 20mm diameter stainless steel grinding balls. As this synthesis is water limited, the same results are not expected for the current synthesis investigation but are used as reference.

EXPERIMENTAL

All materials used for synthesis were industrial grade, so as to ensure that any successes achieved would not only be limited to the laboratory environment. $Mg(OH)_2$ of grade FR-20-200 was sourced from Dead-Sea Periclase, $Al(OH)_3$ of grade RPF-14 was supplied by Chemical Initiatives. Pure hydrotalcite, PURAL MG 63 HT, sourced from Sasol was used as a control sample for test work comparison. All the above materials are of high quality with mostly pure specifications. The $Mg(OH)_2$ was coated with 2% by mass stearic acid, which was removed from before use in the experiment by calcining at a relatively low temperature of $800°C$ for 30 minutes to allow the organic materials to burn off. The calcine step converted the $Mg(OH)_2$ into a mixture of coating-free $Mg(OH)_2$ and light-burned MgO [14].

A Netzsch LME1 horizontal bead mill using 2mm yttrium stabilised zirconia beads was used for the milling of all materials. The mill uses a Watson-Marlow peristaltic pump to pass slurry through the bead mill.

RESULTS AND DISCUSSION

When the calcined $Mg(OH)_2$ (brucite) and $Al(OH)_3$ (gibbsite) materials were combined and milled for 3 hours, the particle size distributions measured at each time interval were generated as shown in Figure 1. Milling of the LDH precursor led to a size distribution over time curve that reached a minimum after 60 minutes and a new maximum after

3 hours of milling. While there is a contamination contribution to the size growth visible from the grey colouration of the white starting materials, it is hypothesised that this size growth is more prominently due to the formation of the LDH crystallites of hydrotalcite and meixnerite. The milled material was hydrothermally aged for 48 hours at 80°C while CO_2 was bubbled through the mixture. The particle size distribution of this aged product is also shown in Figure 1.
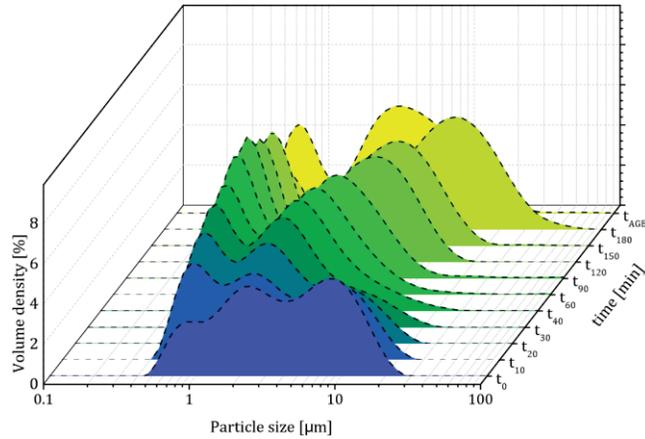
FIGURE 1. Particle size distribution cut sizes of the Mg-Al synthesis precursor after milling over time

From the FT-IR spectra shown in Figure 2, it is clear that a change in chemical species did occur over time. The peak at $3700 cm^{-1}$ associated with the OH stretch in brucite [10] disappeared within 30 minutes of milling. The peaks within the OH stretch region $3400 cm^{-1}$ to $3700 cm^{-1}$ that are associated with the gibbsite lose definition after approximately 60 minutes of milling and form one broad peak in the same range. The peaks within the OH bending region of $1000 cm^{-1}$ disappear after the same amount of time. In addition to the disappearance of all these peaks, a new peak in the range $1300 cm^{-1}$ to $1400 cm^{-1}$ formed as early as 30 minutes and grew in intensity over the duration of the milling and also during the hydrothermal aging step. It is unclear whether this peak is caused by a vibration in the hydroxyl group or the carbonate functional group; both groups have peaks in this region but spectra recorded by Lopez *et al.* [11] , Coates [12] and Palmer, Nguyen, and Frost [10] all seem to suggest that this is the peak of the intercalated carbonate present in hydrotalcite.
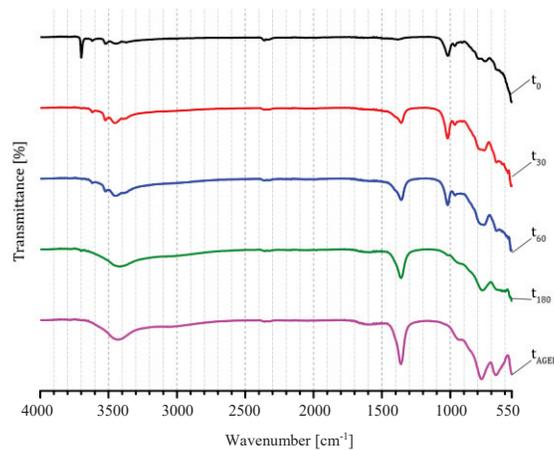
FIGURE 2. IR spectra for the milled Mg-Al precursor over time

All of the above changes in spectra suggest that an LDH was indeed formed, and comparison to the control sample of LDH shown in Figure 3 shows very little difference in FT-IR peak location. As the control LDH was a synthetic hydrotalcite it is believed that the synthesised product is also hydrotalcite.

FIGURE 3. IR spectra comparison of the synthesised LDH (aged) and an industrially supplied LDH (control)

The disappearance of the brucite hydroxide could indicate the partial dissolution of an Mg^{2+} ion to substitute in water molecules and Al^{3+} ions. The disappearance of the gibbsite hydroxide peaks is a clear indication of the amorphatisation and insertion of the aluminium ions into the brucite crystal lattice, and the overall interaction of new double hydroxide complex could explain why the hydroxide peaks become less defined into the final broad hydroxide envelope. The presence of the intercalated carbonate or hydroxide peak also suggests that some type of layered crystal lattice has formed.

The milled samples were analysed with XRD scanning for crystal structure, crystallinity and LDH presence. The results are shown in Figure 4. It can be seen that an LDH crystal is present before milling even began, indicated by the [003] and [006] basal peaks at 13.5° and 27°, but that milling increased the intensity of the LDH peak, which can be associated with an increase in crystallinity and in amount. Another clear indication of the formation of LDH is the presence of the [110] and [112/3] peaks visible in the range of 70° to 80° [13].

FIGURE 4. XRD patterns of the milled synthesis precursor material

The synthesis does appear to be successful, but further analysis of the XRD patterns show that after three hours of milling, there are still brucite and gibbsite crystals present in the mixture. After hydrothermal aging, no gibbsite was detected in the scans but it is hypothesised that the added heat and mixing effects allowed the aluminium to amorphatise completely, making it invisible to the XRD. This is supported by the increase in the broad deviation from the baseline of the XRD pattern (amorphous halo), associated with amorphous material present in the mixture.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained from the milling of magnesium hydroxide and aluminium hydroxide, mechanochemical synthesis of a magnesium aluminium layered double hydroxide was successful, hydrotalcite and meixnerite were both formed in the synthesis. Analysis of the synthesised layered double hydroxide shows that the conversion of the reaction was high but not complete and shows the presence of an amorphous material as well as contamination from the horizontal bead mill itself. The final particle size distribution of the synthesised material after thermal aging is in the range 0.5µm to 12µm. This size distribution is not suitable for shear-intolerant polymer matrix incorporation but after 60 minutes of milling the particle size distribution is in the range 0.5µm to 7µm which is more acceptable for polymer matrix incorporation by heuristic standards of polymer processing.

It is recommended that Mg-Al synthesis experiments be carried out for less than three hours to determine if a smaller particle size distribution and a more LDH-like morphology can be achieved after aging. This is because of the favoured particle size achieved at 60 minutes of milling, however it is not known whether the synthesis is complete after 60 minutes of milling and so further analysis on material at this point in milling is necessary. The total LDH yield should be investigated with Rietveld refinement analysis after autoclaving the synthesised material to crystallise all materials. The optimisation of the Mg-Al mechanochemical synthesis should be investigated to determine if a phase-pure hydrotalcite can be synthesised at a lower cost than the current synthesis methods.

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