The application of focused microwave irradiation coupled with freeze drying to investigate the reaction of MgO and Al₂O₃ slurries in the formation of layered double hydroxides

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Focused microwave irradiation (MI) and freeze drying (FD) techniques have been used to study the generation of layered double hydroxides prepared from MgO–Al₂O₃–H₂O systems. Reactions were undertaken at temperatures of between 100 and 180 °C in order to study the formation of the 3R₁ and 3R₂ polytypes, respectively. MI was found to enhance the rate of formation of both polytypes. FD provided an effective means of quenching the reaction, enabling effective ex situ analysis at intermediate stages. The phase selectivity of the reaction was shown to vary with temperature, promoting the formation of an impurity Mg(OH)₂ at elevated temperatures.

Introduction

Layered double hydroxides (LDHs) are a class of important inorganic lamellar materials which have found applications in many areas, such as catalysis,¹ pharmaceuticals,² and absorbents.³ They have a layered structure similar to that of the mineral brucite (MgOH₂) and have the general formula [M²⁺ₙ₋ₙM³⁺ₙ(OH)₂]ⁿ⁺(A⁻ₓ₋ₙ)ₓ·mH₂O.⁴ Numerous metal (M) and anion (A) combinations have been reported, with the number of potential compositions extremely large.⁴

The performance of an LDH in any given application is dependent both on its composition and chemical structure, properties determined during synthesis. There are several methods of LDH preparation.⁵ The simplest and most commonly used is that of coprecipitation of soluble metal salts. Other routes include hydrothermal synthesis, the sol-gel method and dehydration and reconstruction of a precursor LDH. Additionally, the properties of the LDH are also dependent on the synthesis conditions, including for example pH, temperature, M(II) : M(III) stoichiometry, source of anions and length of reaction.⁶,⁷ Understanding the influence of these parameters is, therefore, becoming increasingly important in order to control and/or tailor the specific properties of the resulting LDH.

Microwave irradiation (MI) is known to enhance the rate of nucleation and growth of crystals in many inorganic reactions, reducing the required synthesis time and resulting in environmental and economic benefits.⁸ The use of MI for LDH synthesis has primarily focused on modifying and improving nucleation and growth properties, when concerned with the precipitation of soluble metal salts.⁹ In this way, crystalline materials with relatively high specific surface area values have been reported. Metals which have been studied include M(II) = Mg, Co, Ni, Cu, Zn, M(III) = Al, Fe, Co, Ga.¹⁰ Carbonate is the most commonly studied anionic species due to its high abundance (from CO₂ uptake) and strong interaction with the surrounding layer. Other anionic species which have been intercalated using MI include chlorides, Evans Blue dye,¹¹ α-naphthaleneacetate,¹² and anthraquinone-2,6-disulfate.¹³ Additionally, MI has been used to prepare PO₄³⁻, P₂O₇⁴⁻,¹⁴ and heteropolyoxometalate pillarared Mg–Al LDHs.¹⁵

In this investigation, we have studied the influence of MI on the reaction of slurries of the MgO–Al₂O₃–H₂O system in the formation of LDHs. This reaction has previously been reported under standard thermal conditions, receiving commercial interest for the preparation of synthetic meixnerite.¹⁶ It also is of interest in the field of green chemistry as water may be used as the solvent and it allows accurate control of the reacting species, thereby reducing waste products.¹⁷ Of particular preparative significance is the dependence of the resulting LDH structure on the synthesis temperature.¹⁸ In this respect, two polytypes, designated by Bookin and Drits as 3R₁ and 3R₂, are known to form depending on the stacking of consecutive layers. The two polytypes may be identified by small shifts in the mid 2θ range (35–55°) of the PXRD pattern.¹⁹ The occurrence of polytypism is important since polytypes may have different physical properties. Anion exchange, for example, may change since the LDH layer–anion interaction strength varies between polytypes due to the change in symmetry of the interlayer sites.²⁰

As most methods of preparation involve water, a drying procedure is required. It is not atypical to read in the literature that samples have been dried in a conventional oven at 70 °C for prolonged periods of time. This will clearly affect the products of the reaction if the reaction has not already reached completion. In this study we report on the use of freeze drying (FD) as a convenient method to quench the reacting slurries, effectively preventing further transformations. The use of FD has enabled ex situ phase analysis at intermediate stages of reaction which is beneficial as the resolution of ex situ analysis is improved.
Experimental details

Slurries of reagent grade MgO (Aldrich) and Cp3 Al2O3 (ALCOA), were prepared with distilled water at the desired stoichiometry (R = [Mg]/[Al] = 2, 5 wt% solids). The Cp3 Al2O3 is an amorphous, γ alumina, prepared by the flash calcination of gibbsite (an amorphous form of alumina was chosen as crystalline Al2O3 is known to be slower to react). The resulting slurries were loaded into 5 ml microwave reaction vials made from borosilicate glass, designed to withstand operating pressures up to 20 bars (300 psi). The reactions were then heated at 100 °C either conventionally (C) in a Carbolite furnace or with MI using an Emrys Synthesizer Optimiser from Biotage. During MI the power level (W) was kept constant. Reactions were also undertaken using MI at 180 °C but it was not possible to achieve the equivalent conventional experiment at this temperature with these reaction vessels. All reactions were undertaken at autogeneous pressure.

After heating for the specified period of time (min) the reaction vessels were cooled within one minute to room temperature under a gas flow. The resultant slurries were then filtered to remove excess water and were then either freeze dried (FD) using a VirTis AdVantage bench top freeze-dryer, or conventionally dried (CD) in an oven at 70 °C. The use of MI during the reaction is seen to significantly increase the rate LDH formation. Strong reflections are visible corresponding well with those in the simulated LDH pattern (MI_10@100_FD and MI_10@180_FD). In contrast, the product resulting from the conventionally heated reaction (C_10@100_FD) exhibits little change from the initial physical mixture. Only a broad, weak reflection, assigned to the 003 basal reflection (2θ ≈ 12°) indicates a small amount of conversion to LDH.

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The | indicates MgO reflection and the △ indicates boehmite reflection. The Physical Mixture plot shows the mixture of MgO and Al2O3 used in the reaction. The C_10@100_FD and MI_10@100_FD patterns are shown for comparison.

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MgO reflections remain visible in the products reacted at 100 °C. These are not observed in the products from reaction at 180 °C, indicating that at this temperature the reaction kinetics are higher, in agreement with expected Arrhenius behaviour.

To study the influence of FD some slurries were dried in a Carbolite furnace at 70 °C for comparison. Fig. 2 shows the PXRD patterns of two furnace dried products collected after 10 minutes of reaction (conventionally, C_10@100_CD and using MI, MI_10@100_CD) at 100 °C. In contrast with the FD products, LDH reflections are clearly visible in the material obtained by conventional reaction. Additionally, no MgO reflections are observed in the product generated using

Results

Nomenclature

The following nomenclature is used in the remainder of this paper: X_t@T_Y, where X = heating method MI or C, t = reaction time (minutes), T = reaction temperature (°C) and Y = drying method FD or CD.

Capturing intermediate stages of reaction

Fig. 1 compares the PXRD patterns of the FD products obtained by conventional and MI heating after 10 minutes of reaction at 100 and 180 °C. The pattern of the initial physical mixture and a simulated pattern of an Mg–Al LDH are shown for comparison.
MI. From these results it could be concluded that the reaction of MgO and Cp3 has reached completion after only 10 minutes of MI at 100°C. This demonstrates the importance of accurately distinguishing the reaction time and avoiding the possibility of further chemical conversion when using ex situ analysis.

At 100°C, only reflections corresponding to reactant MgO and an LDH phase are observed. This is in agreement with the findings of our in situ studies using energy dispersive X-ray diffraction. Any formation of brucite or boehmite, which would be the expected phases formed by the hydration of MgO or Cp3 respectively in this temperature range, are short lived, converting directly into LDH.

At 180°C, however, formation of the impurity brucite is observed (Fig. 1, MI_10@180_FD). This indicates that at this temperature a change in the phase selectivity of the reaction occurs, with the hydration of MgO to Mg(OH)₂ now more favourable.

Characterisation of resultant LDH phases

For reaction times greater than 2 hours, little further change (shifts in reflection positions, identification of new phases etc.) in the products was observed by PXRD, independent of the heating method used. Fig. 3 shows the PXRD patterns and FTIR spectra of the FD products after reaction for 2 hours. Corresponding structural parameters are presented in Table 1. The Scherrer equation was used to estimate the average crystallite size, t, along the c axis by evaluating the full width at half maximum (FWHM) of the basal reflections of the resulting LDH phases. The FWHM were calculated using software installed in the instrument which uses a Gaussian fit. Table 2 compares the t, cₐ and a₀ parameters observed in the LDH products obtained after 10 and 120 minutes of reaction. The values should not be considered as the formal crystallite size as they do not account for line broadening due to stress-related or instrumental effects. Furthermore, the shape of the LDH crystallites is neither spherical nor cubic. As the errors arising due to these assumptions are thought to be similar in all cases the values may be used as a reference to compare samples prepared by different synthetic routes.

The conventional and microwave products from reaction at 100°C are single phase and appear to be isostructural. Observed LDH reflections agree well with the calculated structural parameters for the 3R₁ polytype (where the 012, 015 and 018 reflections are expected to be strong). The a₀ parameters (3.046 and 3.048 Å respectively) also correspond with the expected parameter for an LDH of composition R = 2.25. Reflections in the LDH products prepared by MI are visibly narrower than

Table 1 Observed and calculated structural parameters for the LDH phases observed in Fig. 3

| 2ө₀ | dᵣ₀ | hkl | dᵣ₀ | 2ө₀ | dᵣ₀ | hkl | dᵣ₀ | 2ө₀ | dᵣ₀ | hkl | dᵣ₀ |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 11.728 | 7.540 | 003 | 7.540 | 11.566 | 7.645 | 003 | 7.645 | 12.094 | 7.312 | 003 | 7.312 |
| 34.964 | 2.564 | 012 | 2.569 | 34.820 | 2.574 | 012 | 2.578 | 24.222 | 3.671 | 006 | 3.656 |
| 39.441 | 2.283 | 015 | 2.279 | 39.320 | 2.290 | 015 | 2.288 | 34.228 | 2.618 | 101 | 2.621 |
| 46.801 | 1.939 | 018 | 1.929 | 46.821 | 1.939 | 018 | 1.942 | 34.764 | 2.574 | 012 | 2.567 |
| 52.972 | 1.727 | 1010 | 1.717 | 52.729 | 1.735 | 1010 | 1.731 | 37.898 | 2.372 | 104 | 2.379 |
| 60.789 | 1.523 | 110 | 1.523 | 60.727 | 1.524 | 110 | 1.524 | 44.967 | 2.014 | 107 | 2.019 |
| 62.109 | 1.493 | 113 | 1.493 | 62.016 | 1.495 | 113 | 1.493 | 54.295 | 1.688 | 1010 | 1.687 |
| 69.317 | 1.357 | 003 | 1.357 | 69.228 | 1.360 | 003 | 1.360 | 59.317 | 1.557 | 110 | 1.524 |
| 71.573 | 1.254 | 113 | 1.254 | 71.472 | 1.257 | 113 | 1.257 | 60.713 | 1.524 | 110 | 1.524 |
| 72.159 | 1.220 | 113 | 1.220 | 72.058 | 1.223 | 113 | 1.223 | 62.159 | 1.492 | 113 | 1.492 |

<table>
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<th>Preparation</th>
<th>time/min</th>
<th>c₀/Å</th>
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<td>MI, 180°C</td>
<td>120</td>
<td>22.10</td>
<td>3.06</td>
<td>170</td>
</tr>
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</table>

* No observable LDH reflections in this product.

* sl indicates possible superlattice corresponding to the reflection most commonly expected given by √3×sin60.  b indicates possible brucite reflection.
the reflections in the products from conventional synthesis. The estimated crystallite size of 176 Å for MI is almost double that of the conventional product at 91 Å, which is consistent with the observed increase in the kinetics using this heating method.

At 180 °C, although the PXRD pattern of the product obtained after 2 hours of reaction (Fig. 3, MI_120@180_FD) is similar to the pattern of the product collected after 10 minutes (Fig. 1, MI_10@180_FD), some evidence of further reaction is observed. The relative intensity of brucite compared to LDH reflections has decreased and the LDH reflections have narrowed. After 2 hours of reaction, the LDH reflections in the product correspond well to those previously reported for the 3R2 polytype of LDH, with the expected shifts in the mid 2θ reflections (between 35–55°) clearly visible in the PXRD pattern.18 Observed values of $d_{hkl}$ agree well with those calculated for the 101, 104 and 107 reflections (Table 1), which are expected to be strong in the 3R2 polytype. The estimated crystallite size, 174 Å, is comparable with that of the LDH prepared by MI at 100 °C for the same reaction time (176 Å).

It is interesting to note (from the FTIR data) that the products from reaction at 100 °C contain a band at 1365 cm$^{-1}$, characteristic of the CO$_3^{2-}$ anion. This absorption is not present in the FTIR spectra of the product prepared at 180 °C. It is known that complete elimination of carbonate from LDH is difficult due to the strong affinity of CO$_3^{2-}$ within the interlayer.24 The LDH product resulting from reaction at 180 °C, however, has a 3R2 structure. No LDHs containing CO$_3^{2-}$ are known to exist in this polytype which may be a factor prohibiting uptake of carbonate from atmospheric carbon dioxide.

SEM images of the reactant MgO and Cp3 compared with the materials obtained after 2 hours of reaction are shown in Fig. 4. Clear morphological differences are seen between reactants and products. Large agglomerated particles in which the familiar plate-like morphologies often associated with LDHs can be seen. These particles appear to be less densely agglomerated in the products of reaction at 180 °C (Fig. 4, h and i) compared with those seen in the products from reaction at 100 °C, perhaps indicating less intergrowth of the primary crystallites. In all samples, a wide range of particle sizes are observed. For the product prepared using conventional heating, the plate-like features appear smaller than for the products prepared using MI. This difference in particle size supports the calculated difference estimated using the Scherrer equation.

### Discussion and concluding remarks

MI has been shown to enhance the rate of LDH formation on reaction of the MgO–Al$_2$O$_3$–H$_2$O system, in agreement with the findings of Lim et al.27 Several factors could contribute to the increased rate of reaction observed. Reaction temperatures can be achieved more rapidly using MI, since the MI penetrates the reacting mixture instantaneously providing efficient heat distribution. This reduces any lag time associated with heat conduction through the reaction vessel. Alternatively, increases in rate have also been attributed to the possibility of strong coupling between the MI and certain groups present, such as OH (known as strong absorbers) or have been ascribed to the occurrence of hot spots within the reacting mixture which lead to super heating.28,29

Reaction at 180 °C successfully yielded a 3R2 meixnerite-like LDH after just two hours, much faster than the previously reported conventional synthesis in which reaction times of 24 hours were reported. It was not possible to undertake a conventional synthesis at 180 °C for comparison with the microwave synthesis as the use of a different reaction vessel would have been necessary. Choice of reaction vessel has been observed to influence the reaction between MgO and Cp3 Al$_2$O$_3$, because different vessels have different heating profiles during reaction (depending on their size and thermal mass and the applied heating power).30 The specific thermal conditions created during the reaction are critical in determining both the kinetics and phase selectivity of reaction. This is frequently
observed for systems where the products obtained are dependent on the reaction temperature.\textsuperscript{31,32}

The combination of microwave synthesis and freeze drying has been shown to be an effective approach for avoiding continued secondary reaction. Freeze drying effectively quenches the reaction enabling \textit{ex situ} analysis at intermediate reaction stages. This allows increased sensitivity in phase detection compared to currently used \textit{in situ} analytical techniques, where the presence of water reduces the achievable resolution.

These initial results indicate that increasing the reaction temperature from 100 to 180 °C changes the phase dynamics of the reaction, the hydration of MgO to Mg(OH)\textsubscript{2} becoming more significant at higher reaction temperatures. The morphological differences observed between the products may also have important implications in terms of their chemical reactivity. LDHs are widely used for intercalation chemistry and in the field of catalysis—applications where performance may be limited by the accessible surface area.\textsuperscript{33} Dense aggregation of LDH crystallites by intergrowth may restrict accessibility to the gallery regions, thereby reducing reactivity of these compounds. The crystallite size of an LDH is also known to affect its physical properties, e.g. Albiston et al. reported that the rheology of Mg–Al LDH aqueous dispersions is critically affected by the primary LDH crystal size.\textsuperscript{34}

Acknowledgements

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References