The application of focused microwave irradiation coupled with freeze drying to investigate the reaction of MgO and Al_2O_3 slurries in the formation of layered double hydroxides

Sharon Mitchell, Ian R. Baxendale and William Jones*

Received 24th January 2008, Accepted 25th March 2008
First published as an Advance Article on the web 25th April 2008
DOI: 10.1039/b801365a

Focused microwave irradiation (MI) and freeze drying (FD) techniques have been used to study the generation of layered double hydroxides prepared from $MgO–Al_2O_3–H_2O$ systems. Reactions were undertaken at temperatures of between 100 and 180 °C in order to study the formation of the $3R_1$ and $3R_2$ 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 ($MgOH_2$) and have the general formula $[M^{2+}_{1-n}M^{3+}_{n}(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$.[3] 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 CO_2 uptake) and strong interaction with the surrounding layer. Other anionic species which have been intercalated using MI include chlorides, Evans Blue dye,[11] α-napthaleneacetate,[12] and anthraquinone-2,6-disulfate.[13] Additionally, MI has been used to prepare PO_4^{3-}, $P_2O_7^{4-}$,[14] and heteropolyoxometalate pillared Mg–Al LDHs.[15]

In this investigation, we have studied the influence of MI on the reaction of slurries of the $MgO–Al_2O_3–H_2O$ 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 dependance of the resulting LDH structure on the synthesis temperature.[18] In this respect, two polytypes, designated by Bookin and Drits as $3R_1$ and $3R_2$, are known to form depending on the stacking of consecutive layers. The two polytypes may be identified by small shifts in the mid 2 theta 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

---

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, Cambridgeshire, UK. E-mail: wj10@cam.ac.uk; Fax: +44 (0)1223 336017; Tel: +44 (0)1223 336468

compared to the *in situ* approaches such as energy dispersive X-ray diffraction that have previously been applied.[21]

Experimental details

Slurries of reagent grade MgO (Aldrich) and Cp3 Al_2O_3 (ALCOA), were prepared with distilled water at the desired stoichiometry (R = [Mg]/[Al] = 2, 5 wt% solids). The Cp3 Al_2O_3 is an amorphous, γ alumina, prepared by the flash calcination of gibbsite (an amorphous form of alumina was chosen as crystalline Al_2O_3 is known to be slower to react).[22] 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).[23] 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 a furnace at 70 °C. During the freeze drying process the product was cooled to −40 °C, and held at this temperature under reduced pressure for 2 hours. The shelf temperature was then gradually raised to room temperature over a further 4 hour period.

Powder X-ray diffraction (PXRD) patterns of the resultant materials were then recorded using a Philips PW3710 diffractometer in reflection geometry using graphite monochromated Cu Kα radiation. Data were collected from finely ground samples pressed on a flat plate, glass sample holder. Phase identification was achieved by comparison with PXRD patterns simulated, using the X'Pert Plus software, from single crystal structural information data obtained from the International Crystal Structure Database (Numbers: brucite No. 95475, boehmite No. 59608, MgO periclase No. 95468).

Fourier transform infra-red (FTIR) spectra were recorded on a ThermoNicolet Nexus Spectrometer using the Smart Golden Gate single reflection stage attenuated total reflection. A background spectrum was recorded before the sample was placed on the sample stage, pressure applied and data acquired. Data were recorded in the range ν = 550–3800 cm^{-1}.

Scanning electron microscopy (SEM) was undertaken using a JEOL 5800LV instrument. Samples were dispersed from ethanol onto a freshly cleaved mica surface. A thin platinum coating was applied to reduce the effects of sample charging.

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[24] are shown for comparison.

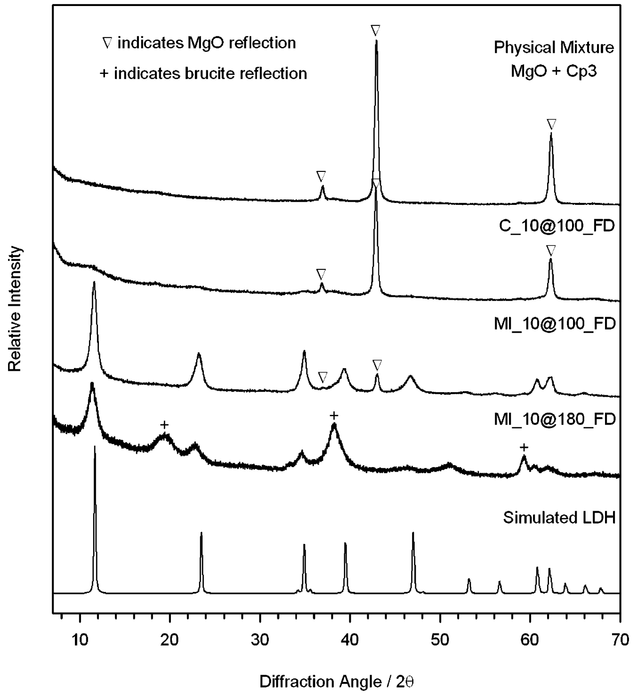

Fig. 1 PXRD patterns of the FD products obtained after 10 minutes of reaction compared with the PXRD pattern of the initial physical mixture and a simulated PXRD pattern of an Mg–Al LDH.

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 ($2\theta \approx 12°$) indicates a small amount of conversion to LDH.

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

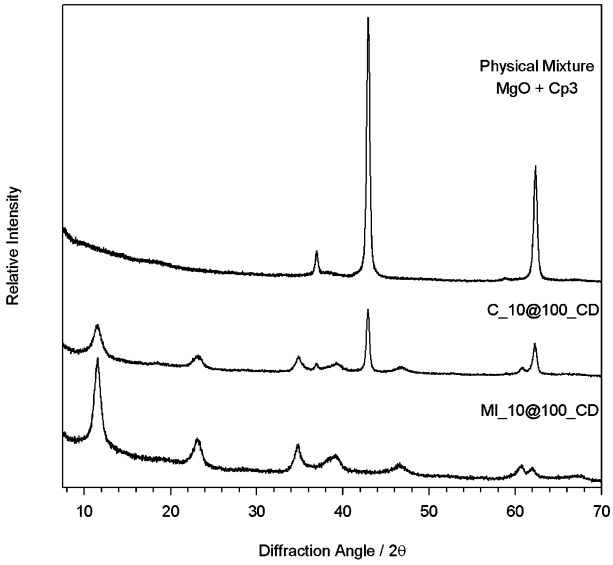

Fig. 2 PXRD patterns of products from slurries reacted for 10 minutes at 100 °C using (a) conventional and (b) MI heating, furnace dried at 70 °C. The PXRD pattern of the initial physical mixture is also shown.

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.[21] 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*, c_o and a_o 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.[25] 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 $3R_1$ polytype (where the 012, 015 and 018 reflections are expected to be strong). The a_o parameters (3.046 and 3.048 Å respectively) also correspond with the expected parameter for an LDH of composition $R = 2$.[26] Reflections in the LDH products prepared by MI are visibly narrower than

Table 2 Summary of estimated crystallite size (*t*) and structural parameters (c_o and a_o) for LDH phases obtained

Preparation	time/min	c_0/Å	a_0/Å	*t* (003)/Å
Conventional, 100 °C	10	—[a]	—[a]	—[a]
Conventional, 100 °C	120	22.62	3.05	90
MI, 100 °C	10	23.05	3.05	70
MI, 100 °C	120	22.94	3.05	170
MI, 180 °C	10	23.27	3.06	80
MI, 180 °C	120	22.10	3.06	170

[a] No observable LDH reflections in this product.

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

(a) C_120@100_FD				(b) MI_120@100_FD				(c) MI_120@180_FD			
$2\theta_{obs}$	d_{obs}	*hkl*	d_{calc}	$2\theta_{obs}$	d_{obs}	*hkl*	d_{calc}	$2\theta_{obs}$	d_{obs}	*hkl*	d_{calc}
11.728	7.540	003	7.540	11.566	7.645	003	7.645	12.094	7.312	003	7.312
23.393	3.800	006	3.770	23.231	3.826	006	3.823	19.390	4.574	sl[a]/b[b]	4.573
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
								59.317	1.557	b[b]	
								60.713	1.524	110	1.524
								62.159	1.492	113	1.492
a_0	3.046	c_o	22.620	a_0	3.048	c_0	22.935	a_0	3.054	c_0	22.098

[a] sl indicates possible superlattice corresponding to the reflection most commonly expected given by $\sqrt{3}a\sin60$. [b] b indicates possible brucite reflection.

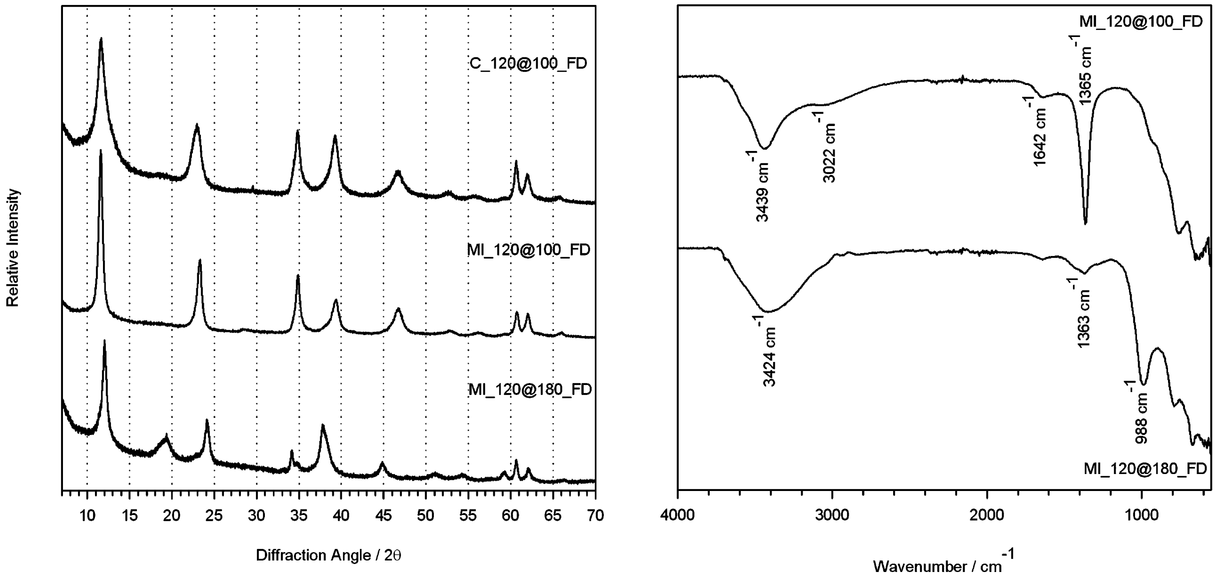

Fig. 3 PXRD patterns (left) and corresponding FTIR spectra (right) of products obtained after 2 hours of reaction at 100 °C (both conventionally and using MI) and at 180 °C using MI.

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 $3R_2$ 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 $3R_2$ 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 $3R_2$ 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 $MgO–Al_2O_3–H_2O$ 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 $3R_2$ 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_2O_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

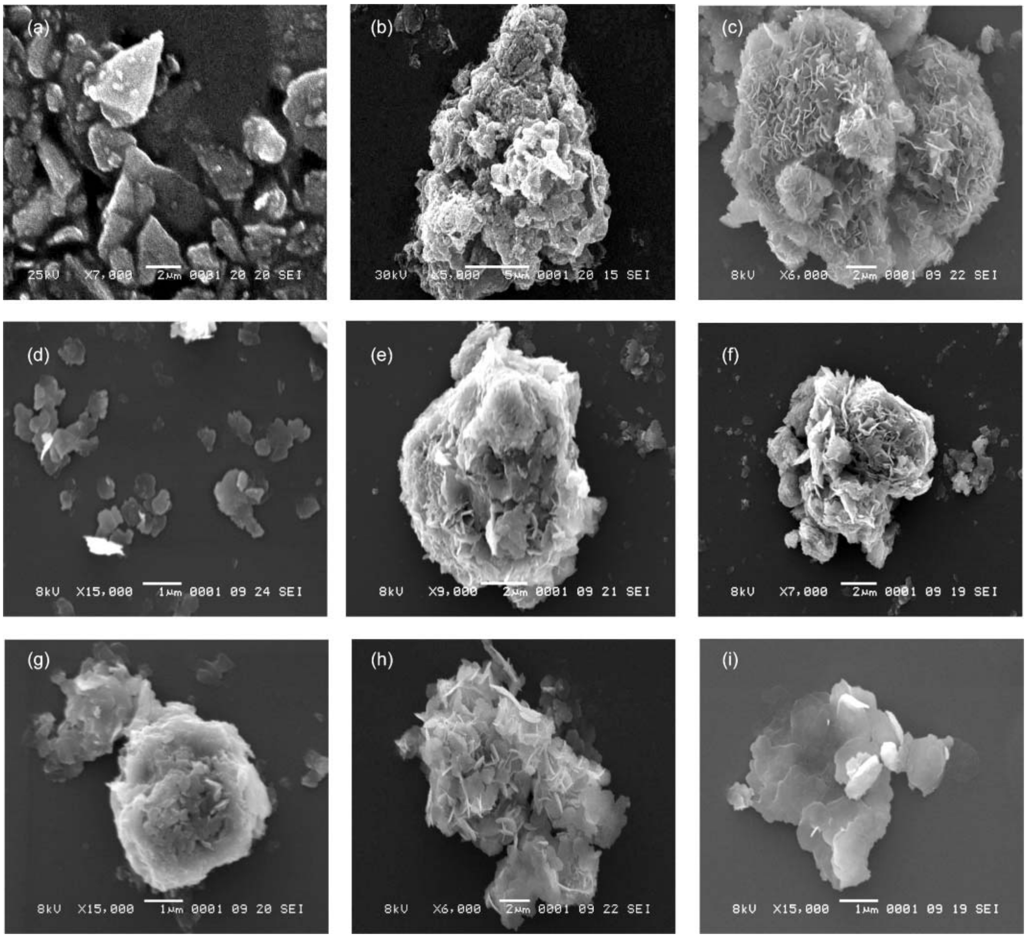

Fig. 4 SEM images of reactant (a) MgO and (b) Cp3 Al_2O_3 compared with those of the products, (c and d) C_120@100_FD, (e, f and g) MI_120@100_FD and (h and i) MI_120@180_FD.

observed for systems where the products obtained are dependent on the reaction temperature.[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 *ex situ* analysis at intermediate reaction stages. This allows increased sensitivity in phase detection compared to currently used *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 $Mg(OH)_2$ 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.[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.[34]

Acknowledgements

We would like to thank EPSRC for funding.

References

1 D. Tichit and B. Coq, *Catal. Technol.*, 2003, **7**, 206.
2 J-H. Choy, S-J. Choi, J-M. Oh and T. Park, *Appl. Clay Sci.*, 2007, **36**, 122.
3 A. Roy, C. Forano, J. P. Besse, in *Layered Double Hydroxides: Present and Future*, ed. V. Rives, Nova Sci, Pub., 2001, ch.1, pp. 1.
4 D. G. Evans, R. C. T. Slade, in *Layered Double Hydroxides, Structure and Bonding*, ed. X. Duan and D. G. Evans, Springer-Verlag, Berlin, 2006, vol. 119, ch.1, pp. 1-87.
5 D. G. Evans and X. Duan, *Chem. Commun.*, 2006, **5**, 485.
6 J. W. Boclair and P. S. Braterman, *Chem. Mater.*, 1999, **11**, 298.
7 G. Mascolo, *Appl. Clay Sci.*, 1995, **10**, 21.
8 K. J. Rao, B. Vaidhyanathan, M. Ganguli and P. A. Ramakrishnan, *Chem. Mater.*, 1999, **11**, 882.
9 S. Kannan and R. V. Jasra, *J. Mater. Chem.*, 2000, **10**, 2311.
10 D. Tichit, A. Rolland, F. Prinetto, G. Fetter, M. D. Martinez-Ortiz, M. A. Valenzuela and P. Bosch, *J. Mater. Chem.*, 2002, **12**, 3832.
11 M. Z. bin Hussein, A. H. Yahaya; and L. M. Ping, *Dyes Pigm.*, 2004, **63**, 135.
12 M. Z. bin Hussein, Z. Zainal, A. H. Yahaya and D. W. V. Foo, *J. Mater. Synth. Process.*, 2002, **10**, 89.
13 M. Z. bin Hussein, Z. Zainal, T. Y. Hin and O. W. Tat, *J. Microwave Power Electromagnetic Energy*, 2001, **36**, 113.
14 Z. J. Zhang, B. Lan, L. R. Feng, S. J. Lu and F. L. Qiu, *J. Inorg. Mater.*, 2004, **19**, 761.

15 Z. Xu, Y. Wu, H. He and D. Jiang, *Stud. Surf. Sci. Catal.*, 1994, **90**, 279.
16 E. S. Martin and A. Pearson, *US Pat.*, 5 514 361, 1996.
17 H. C. Greenwell, W. Jones, D. N. Stamires, P. O'Connor and M. F. Brady, *Green Chem.*, 2006, **8**, 1067.
18 S. P. Newman, W. Jones, P. O'Connor and D. N. Stamires, *J. Mater. Chem.*, 2002, **12**, 153.
19 A. S. Bookin and V. A. Drits, *Clays Clay Miner.*, 1993, **41**, 551.
20 V. Radha, P. Vishnu Kamath and C. Shivakumara, *J. Phys. Chem. B*, 2007, **111**, 3411.
21 S. Mitchell, T. Biswick, W. Jones, G. Williams and D. O'Hare, *Green Chem.*, 2007, **9**, 373.
22 D. M. Roy, R. Roy and E. F. Osborn, *Am. J. Sci.*, 1953, **251**, 337.
23 Standard 5 ml vials commercially available from Biotage AB, http://www.biotage.com.
24 M. Belloto, B. Rebours, O. Clause, J. Lynch, D. Bazin and E. Elkaim, *J. Phys. Chem.*, 1996, **100**, 8527.
25 P. Benito, F. M. Labajos, J. Rocha and V. Rives, *Microporous Mesoporous Mater.*, 2006, **94**, 148.
26 M. Kaneyoshi and W. Jones, *J. Mater. Chem.*, 1999, **9**, 805.
27 H. M. Lim, M. R. Kang, S. C. Lee, S-H Lee and K. J. Kim, *Mater. Sci. Forum*, 2005, **492–493**, 743.
28 F. J. Berry, L. E. Smart, P. S. Sai-Prasad, N. Lingaiah and P. Kanta-Rao, *Appl. Catal., A*, 2000, **204**, 191.
29 E. Reguera, C. Diaz-Aguila and H. Yee-Madeira, *J. Mater. Sci.*, 2005, **40**, 5331.
30 R. Hoogenboom, R. M. Paulus, A. Pilotti and U. S. Schubert, *Macromol. Rapid Commun.*, 2006, **27**, 1556.
31 W. Sun and J. Li, *Mater. Lett.*, 2006, **60**, 1599.
32 Y. C. Chua and X. Lu, *Langmuir*, 2007, **23**, 1701.
33 M. Adachi-Pagano, C. Forano and J. P. Besse, *J. Mater. Chem.*, 2003, **13**, 1988.
34 L. Albiston, K. R. Franklin, E. Lee and J. B. A. F. Smeulders, *J. Mater. Chem.*, 1996, **6**, 871.