Reversible thermal behavior of the layered double hydroxide of Mg with Al: mechanistic studies

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The layered double hydroxide (LDH) of Mg with Al decomposes at 450 °C to yield a mixed metal oxide. The oxide reconstructs back to the parent LDH either on cooling in air or soaking in water. This reversible thermal behaviour was attributed to the formation of an unstable defect rocksalt phase (comprising Al^{3+} ions partially substituting for Mg^{2+} in MgO) on decomposition of the LDH. However a simple oxide mixture of MgO and Al_2O_3 taken in the 6 : 1 molar ratio is also found to yield a LDH-like phase when soaked in an aqueous solution of a suitable anion, suggesting that the reconstruction occurs through a simple dissolution–reprecipitation mechanism. The formation of the defect rocksalt phase is not a necessary precondition for reconstruction. However, the kinetics of the reconstruction reaction depends upon the nature of the anion and the thermal history of the oxides. The presence of carbonate ions and unsintered oxides hastens the reconstruction reaction.

Introduction

Hydrotalcites (HT), $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$ ($x = 0.2$–0.33, $m = 0.66$–0.75), and their transition metal analogues decompose at moderate temperatures (450–650 °C) to yield mixed metal oxides, which are used as catalysts for a number of base catalyzed reactions.[1] Many of the hydrotalcite-like LDHs, notably the Mg–Al[2] and the Zn–Al[3] systems, are known to reconstruct back when their oxide residues obtained from thermal decomposition are suspended in water. The Mg–Al system is especially remarkable, as the oxide residues undergo reconstruction, even on standing in air, by the absorption of CO_2 and H_2O from the atmosphere.[4,5] The reversible thermal behavior of the hydrotalcites has been studied by TG,[4] MAS-NMR[5,6] and variable temperature XRD.[7]

As this reversible behavior is exhibited by only a few LDHs, it would be interesting to know if this behaviour is caused by (i) the trivalent ion content, (ii) the nature of the divalent ion, (iii) the nature of the intercalated anion and/or (iv) the thermal history of the oxide.

We undertook a series of investigations to examine the origin of the reversible thermal behavior of the hydrotalcites and to investigate the mechanism of reconstruction.

Experimental

Mg–Al carbonate LDHs with various Al contents ($x = 0.15$–0.35) and Mg–Al sulfate with $x = 0.25$ were prepared by Reichle's method.[8] The Mg and Al contents of a few selected samples were determined by wet chemical analysis (gravimetric procedures for two metal constituents[9]). The expected (based on the proportion of salts used for coprecipitation) and observed metal contents agreed reasonably well.[4] For instance, when the expected composition was $x = 0.25$, in the present study, that observed was $x = 0.253$. We therefore refer to all the LDHs by their nominal composition.

$Mg(OH)_2$ was precipitated from a magnesium nitrate solution using alkali. $Al(OH)_3$ was precipitated from an aluminium nitrate solution using ammonia. The hydroxides of Mg and Al were fired at 600 °C for 18 h to obtain the corresponding oxides.

LDHs of different compositions were heated to 650 °C in a thermogravimetric balance (lab-built system, heating rate 5 °C min^{-1}). At this temperature, the weight loss reached a limiting value and corresponded to that expected from a complete decomposition reaction.[4] In this paper, we examine the rehydration behaviour of three kinds of samples.

(1) The oxide residues obtained by thermal decomposition of the LDHs. These have been labeled as samples A and A' to indicate that they have been derived from CO_3^{2-} and SO_4^{2-}-containing LDHs, respectively.

(2) A mixture of MgO and Al_2O_3 (molar ratio 6 : 1), obtained by simply grinding the two oxides together, is labeled as sample B.

(3) A calcined Mg–Al oxide, compositionally equivalent to the "defect rocksalt", $Mg_{1-x}Al_{2x/3}\square_{x/3}O$, was obtained by heating a 6 : 1 (molar ratio) mixture of MgO and Al_2O_3 at 800 °C for 18 h with intermittent grinding. This oxide is labeled as sample C.

Samples A, derived from LDHs of different compositions, were exposed to ambient air for 3 days, by which time they regained 100% of the lost weight. Sample A' did not regain all the lost weight on standing in ambient air. It was soaked in a 0.5 M Na_2SO_4 (or Na_2CO_3) solution at 65 °C for 5 days.

Approximately 500 mg of each of samples B and C were soaked in 50 ml of 0.5 M Na_2CO_3 solution at 65 °C for 5 days. The products were washed free of ions, filtered and dried at 100 °C to constant weight. Sample C was also subjected to hydrothermal treatment in 0.5 M Na_2CO_3 (115 ml) in a Teflon-lined stainless steel autoclave (volume 150 ml) at 160 °C for 24 h.

All the samples were characterized by powder X-ray diffraction (JEOL JDX8P powder diffractometer, Cu-Kα $\lambda = 1.541$ Å or Co-Kα $\lambda = 1.79$ Å) and infrared spectroscopy (Nicolet Model Impact 400D FTIR spectrometer, KBr pellets, 4 cm^{-1} resolution). The surface areas of samples A, B and C were measured using a NOVA 1000 Ver. 3.70 high speed gas sorption analyzer. Electron microscopy was carried out with a JEOL JEM 200 CX electron microscope operating at 200 kV. The powder samples were dispersed on carbon grids (mesh size 200).

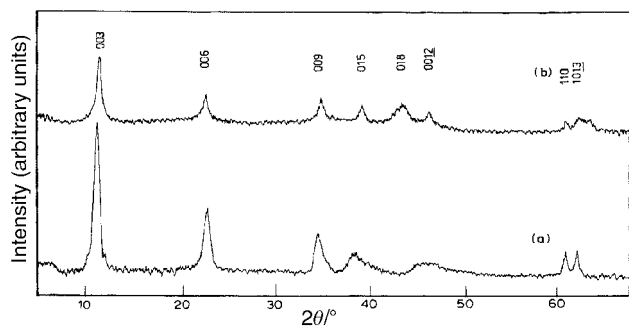The reversibility of the thermal behaviour of the LDHs was

Fig. 1 Powder X-ray diffraction patterns (source, Cu-Kα) of the as-prepared Mg–Al carbonate ($x = 0.25$) LDH (a) and the material obtained when sample A was exposed to air for 3 days (b).
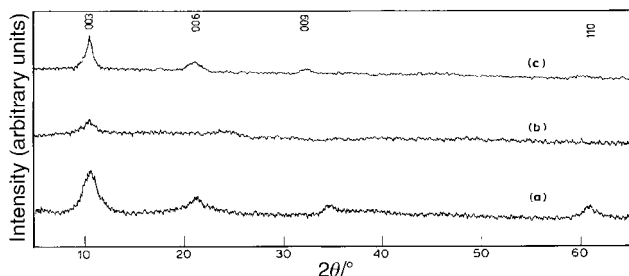

Fig. 2 Powder X-ray diffraction patterns (source, Cu-Kα) of the as-prepared Mg–Al sulfate ($x = 0.25$) LDH (a) and the materials obtained when sample A′ was soaked in 0.5 M sodium sulfate solution for 3 days at ambient temperature (b) and 65 °C (c).

Fig. 3 IR spectrum of the sample A′.

determined by the following criteria: (i) The oxide residue obtained from thermal decomposition should regain at least 95% of the original weight on rehydration. (ii) The PXRD pattern of the hydrated sample must exhibit the reappearance of the lines due to the (00*l*) reflections, especially the low angle reflection at approx. 7.6 Å.

A greater emphasis has been laid on the (00*l*) reflections, as the LDHs are essentially layered clay-like materials containing intercalated anions. In the present study, the anions used are carbonates and sulfates. In the absence of intercalated anions, the expected interlayer distance is only 4.6 Å, as in $Mg(OH)_2$. The low angle reflection is therefore the signature of the LDH. Furthermore, the low angle reflection is accompanied by the appearance of higher order reflections, a characteristic of layered clays.[10] We do not attach much importance to the appearance of the (110) reflection, as reconstructed and anion exchanged LDHs are known to exhibit turbostratic disorder,[11] which destroys the line shape of all (*hk*0) reflections.[12]

Results and discussion

In the Mg–Al carbonate system, LDHs of all compositions ($x = 0.15$–0.35) underwent reconstruction to give HT-like phases when the products of thermal decomposition (samples A) were left exposed to air for 3 days. On soaking in a Na_2CO_3 solution, the reconstruction is complete in less than 5 h. It is clear that the Al content is not a determining factor for reversible thermal behaviour. Typical results are shown in Fig. 1, where the PXRD pattern of the as-prepared Mg–Al LDH ($x = 0.25$) is compared with that of the reconstructed material. The reconstruction phenomenon is self-evident. The observations are in agreement with previous reports.[2,4] It has been proposed that the oxide residue obtained on thermal decomposition of the hydrotalcites comprises a defect rocksalt phase, $Mg_{1-x}Al_{2x/3}\square_{x/3}O$, which, being unstable, causes the rapid reconstruction of the parent hydroxide.[2] When the oxide residue is sintered at temperatures higher than 1100 °C,
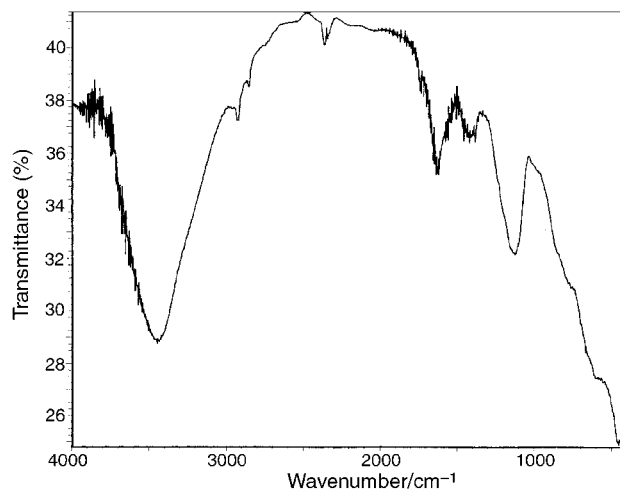
irreversible spinel ($MgAl_2O_4$) formation is observed and no reconstruction of the hydroxide phase occurs thereafter.[2]

The LDH structure is based on that of the mineral brucite. Therefore, the LDH→defect rocksalt conversion, like the brucite→rocksalt conversion,[13] is expected to be topotactic in nature, with the $(001)_{LDH} \parallel (111)_{rocksalt}$. The reconstruction of the parent phase can therefore take place by two possible mechanisms: (i) by the insertion of protons/hydroxyl ions at the defect sites of the oxide or (ii) by a dissolution–reprecipitation process.

The only LDHs that exhibit reconstruction appear to be those containing either Mg or Zn. The hydroxides of these metals have relatively high solubility in aqueous solutions. This throws up the possibility that reconstruction occurs *via* dissolution–reprecipitation of the oxide residue obtained by decomposition. In such a case, the defect rocksalt phase is unnecessary for the reconstruction reaction.

In order to verify whether the defect rocksalt phase is essential for the reconstruction reaction we carried out reconstruction studies on the Mg–Al sulfate system. Unlike the carbonate anion, the sulfate anion does not undergo decomposition. It is therefore expected that a part of the Al content of the LDH would phase-separate as $Al_2(SO_4)_3$ and not be incorporated in the MgO. This would naturally suppress the formation of the defect rocksalt phase. In Fig. 2, the PXRD patterns of the as-prepared Mg–Al sulfate LDH ($x = 0.25$) and the products of the reconstruction reaction [0.5 M Na_2SO_4 solution, 72 h, at (i) ambient temperature and (ii) 65 °C] are shown. The oxide residue prior to reconstruction (sample A′) was found to be X-ray amorphous. However, the IR spectrum of this sample shows the characteristic absorption at 1129 cm^{-1} due to sulfate ions (Fig. 3) suggesting the presence of $Al_2(SO_4)_3$ and, hence, the possible suppression of the defect rocksalt phase. Thermogravimetic data (not presented here) also point to the retention of the sulfate ions in the residue. Reconstruction does not take place satisfactorily at ambient temperature (Fig. 2b), but is significant at 65 °C (Fig. 2c).

From these results we conclude that (i) the defect rocksalt phase is not essential to carry out reconstruction, (ii) the defect rocksalt phase can, however, hasten the process and (iii) the reconstruction occurs *via* a dissolution–reprecipitation pathway.

If this is the case, a simple mixture of MgO and Al_2O_3 (sample B) should itself yield the LDH phase when soaked in an aqueous solution of a suitable anion! The PXRD pattern of the oxide mixture shows the reflections of MgO, the Al_2O_3 being X-ray amorphous. Fig. 4 shows the PXRD pattern of a mixture of MgO and Al_2O_3 (sample B) and that of the product
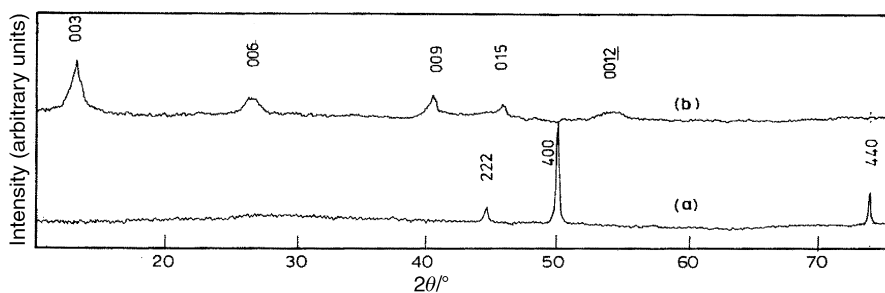
Fig. 4 Powder X-ray diffraction pattern (source, Co-Kα) of sample B (a), compared with that of the material obtained when sample B was soaked in 0.5 M sodium carbonate solution for 5 days at 65 °C (b).
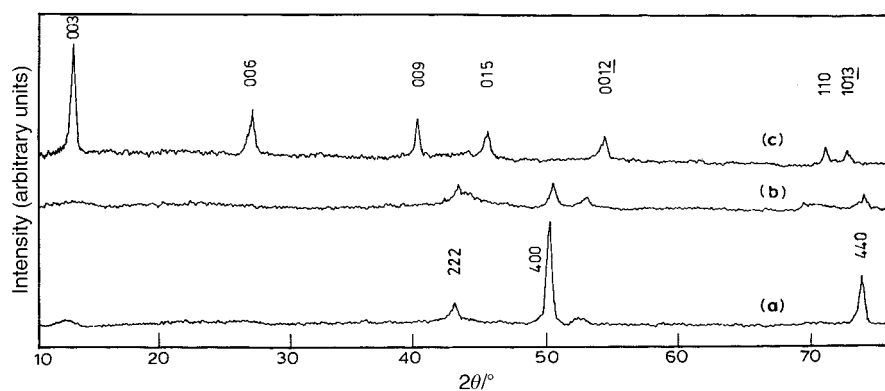

Fig. 5 Powder X-ray diffraction patterns (source, Co-Kα) of sample C (a) and the materials obtained when sample C was soaked in 0.5 M sodium carbonate solution for 5 days at 65 °C (b) and hydrothermally treated in 0.5 M sodium carbonate solution for 24 h at 160 °C (c).
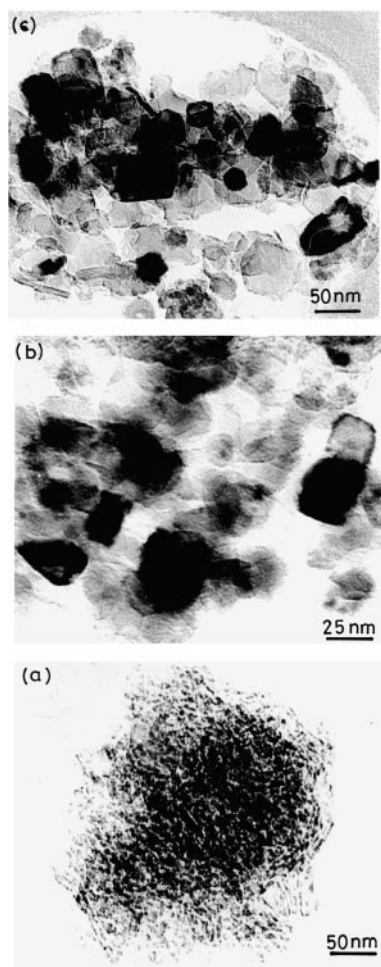

Fig. 6 Scanning electron micrographs of the samples A (a), B (b) and C (c).

obtained when this mixture was soaked in a carbonate solution (65 °C, 5 days). The observed pattern matches well with that of a LDH-like phase. This further confirms that the reconstruction of the LDH proceeds through a dissolution–reprecipitation process and that the defect rocksalt is not necessary.

In order to verify whether the kinetics of the reconstruction process are affected by the defect rocksalt phase, we synthesized the defect rocksalt by reacting MgO and Al$_2$O$_3$ at 800 °C (sample C)—a temperature high enough to allow diffusion and sintering, but low enough to avoid formation of the spinel, MgAl$_2$O$_4$. The PXRD pattern of this defect oxide material along with those of the products obtained by soaking it in a carbonate solution for 5 days and hydrothermally treating it (160 °C, 24 h) are shown in Fig. 5. While simple soaking in carbonate solution yields only a poorly crystalline oxide phase, the LDH is obtained upon hydrothermal treatment. This suggests that the defect oxide phase obtained by the ceramic process retards the reconstruction reaction, while that obtained by LDH decomposition at low temperatures (650 °C) exhibits the most facile reconstruction. The differences in the rates of formation of the HT phase in all these cases were found to vary due to particle size effects.

Fig. 6 shows TEM images of samples A, B and C. Sample A is nanoparticulate and the ill-defined agglomerates have an estimated particle size in the 33–50 Å range. Samples B and C, obtained from a mixture of the oxides of Mg and Al, are somewhat similar and contain particles with a well-defined rectangular morphology. The particle size is in the 550–600 Å range. The surface area measurements also indicate a similar trend. The specific surface areas of samples A, B and C were found to be 189, 71 and 51 m^2 g^{-1} respectively. The reactivities of these samples towards LDH formation vary inversely with particle size and directly with the surface area. All these observations indicate that the reconstruction reaction of the LDH proceeds *via* a simple dissolution–reprecipitation mechanism.

Conclusions

In conclusion, the reconstruction behaviour of the LDHs is linked to the solubility of the divalent metal hydroxide in water. Reconstruction to the LDH phase occurs by a simple dissolution–reprecipitation mechanism. Reconstruction is facile when unsintered oxides are used in the presence of the carbonate anions. The unsintered oxide could be a defect rocksalt or just a mixture of the unary oxides.

Acknowledgements

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