Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Layered Double Hydroxide Intercalate of Metal-Chelate Complex—a Novel Precursor for the Formation of a Mixed Metal Oxide

Masami Kaneyoshi [a] & William Jones [a]

[a] University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, U.K.

Version of record first published: 24 Sep 2006

To cite this article: Masami Kaneyoshi & William Jones (2001): Layered Double Hydroxide Intercalate of Metal-Chelate Complex—a Novel Precursor for the Formation of a Mixed Metal Oxide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 459-468

To link to this article: http://dx.doi.org/10.1080/10587250108023724

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 459-468
Reprints available directly from the publisher
Photocopying permitted by license only

Layered Double Hydroxide Intercalate of Metal-Chelate Complex – a Novel Precursor for the Formation of a Mixed Metal Oxide

MASAMI KANEYOSHI and WILLIAM JONES

University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, U.K.

The reaction of a nitrilotriacetate-intercalated Mg-Al layered double hydroxide in a lanthanum nitrate solution is studied. La^{3+} is incorporated into the interlayer through the formation of a chelate complex. NO_3^- is also taken up as a charge-balancing anion. During chelation the interlayer repeat increases from 11.9 A to 13.9 A. Chemical analysis suggests that 1:1 and 1:2 metal:chelate complexes are formed within the interlayer. Calcination of the La^{3+}-containing double hydroxide results in the formation of $LaAlO_3$.

Keywords: Intercalation; LDH; Anionic clay; Chelate; Lanthanum Oxide; Thermal decomposition

INTRODUCTION

Layered double hydroxides (LDHs) are materials that have recently received attention because of their potential application as catalysts, sorbents, antacids etc.[1-3] They may be represented by the general formula $[M^{2+}_{1-x}\ M^{3+}_{x}\ (OH)_2][\ A^{n-}\ mH_2O]$, where M^{2+} and M^{3+} are

divalent and trivalent cations, respectively; x is equal to the ratio $M^{3+}/(M^{2+}+M^{3+})$ and A^{n-} is an exchangeable anion of charge n. Structurally, the metal cations form positively charged, brucite-like layers, with the anion and water present in the interlayer region.[4,5]

As a result of the attractive properties of the mixed oxides obtained following calcination, LDHs are already industrially employed as precursors of catalysts or catalyst supports[2] The range of cations present within the layers includes Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} $Cd^{2+}$and Al^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+}. The properties of these materials have been extensively studied.[1,2] Preparation has also been reported in which all the M^{3+} was Sc[6], Mn[7] or V[8]. In addition, it has also been reported that a component of the cations within a Mg-Al LDH may be replaced by Rh or Ru.[9] Some of these studies have been aimed at the homogeneous or sub-nano level mixing of two or more kind of metal oxides.

It is likely to be difficult, however, to prepare a LDH that contains a large amount of a M^{3+} cation with a relatively large ionic radius (e.g. Y, La, Bi etc.). Fernández et al. studied the synthesis of a Mg-Al-Y containing LDH and reported that when the Y/Al ratio increased to a value close to 0.8, the crystallinity of the material was considerably decreased.[10]

A possible alternative to the preparation of homogeneous mixtures of three or more different metal oxides, including large M^{3+} cations, is to use LDHs intercalated with a negatively charged metal complex as a precursor. As an example of the anionic complexes intercalated into LDHs, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$,[11] $Ru(BPS)_3^{4-}$ (BPS : 4,7-diphenyl-

1,10-phenanthrolinedisulphonate),[12] and Cu-phthalocyaninetetrasulphonate[13] have been reported.

In a recent paper we reported on the formation of Mg-Al LDHs intercalated with nitrilotriacetate (NTA) anions, such anions having the capacity to chelate various metals.[14] In this paper we describe the incorporation of La^{3+} ions into a pre-formed NTA-intercalated Mg-Al LDH. It is known that La and NTA forms 1:1 and 1:2 complexes in aqueous solution.[15] We show how this complex formation also operates in the incorporation of La^{3+} into the interlayer. We also report on the calcination behaviour of the (La, NTA) intercalated LDH and the nature of the metal oxides that result.

EXPERIMENTAL

Preparation of the NTA-intercalated LDH (NTA-LDH)

Several procedures for the preparation of NTA-intercalated Mg-Al LDHs have been described.[14] In this work we employed the anion-exchange method. 2.5 mmol of the trisodium salt of NTA and 1.5 mmol of the free acid of NTA were dissolved into 100 ml of water (pH = 3.4). To this solution, 3.11 g of a nitrate-containing LDH (Mg/Al = 1.87, containing 0.012 mol Al) was dispersed and stirred under a continuous flow of N_2 at room temperature for three hours (during this time the solution pH increased to 8.3). The slurry was filtered, washed with deionised water and dried in an oven at 65 °C in air.

Incorporation of La into the NTA-intercalated LDH

NTA-intercalated LDH containing approximately 1 mmol of NTA was added to 50 ml of 0.02M lanthanum nitrate solution (pH adjusted to 8.5 by addition of NH_3aq). The slurry was stirred (under a flow of N_2 to minimise CO_2/carbonate interference) at 65 °C for four hours (final pH = 8.2). The slurry was then filtered, washed with deionised water and dried in an oven (65 °C) in air.

Calcination of the (La, NTA) intercalated LDH

The (La, NTA) intercalated LDH was calcined in air at 500, 800 and 1100 °C for five hours.

Comparative solid-state reaction

MgO, Al_2O_3 and La_2O_3 (molar ratio 1.61 / 1 / 0.300 i.e. the same as the composition of the (La, NTA) intercalated LDH) were mixed in a mortar with ethanol. The mixture was dried and calcined in air at 1100 °C for five hours.

Sample characterisation

Chemical analysis of C, H and N was carried out using an Exeter Analytical CE-400 Elemental Analyser. Al, La and Mg were analysed by ICP-AES using a SEIKO SPS4000 spectrophotometer. Weight loss on ignition at 1000°C was also used to provide information concerning chemical composition. Powder X-ray diffraction (PXRD) data was obtained using a Phillips PW1710 diffractometer with Cu Kα radiation with a Ni filter for Kβ attenuation. A step scan of 0.04° 2θ holding 1.5 s at each step was used. Fourier transform infrared (FT-IR) spectra were

recorded with a Perkin-Elmer Paragon 1000 spectrometer using the KBr pellet technique.

RESULTS AND DISCUSSION

Reaction of the NTA-intercalated LDH and $La(NO_3)_3$

The chemical analysis results (Table 1) show that a considerable amount of La is incorporated into the LDH. In addition, the nitrogen content of material also increases as a result of the contact of the NTA-LDH with the La nitrate solution.

Table 1 Chemical analysis data for the NTA-LDH and the La-incorporated NTA-LDH.

Sample	Molar ratio Mg / Al	La / Al	C (%)	N (%)	LoI[a] (%)
NTA-LDH	1.86	-	7.53	1.91	48.62
(La, NTA)-LDH	1.61	0.300	6.22	2.97	48.60

a : Weight loss following calcination at 1000 °C
Possible chemical formula for the starting NTA-LDH: $[Mg_{0.65}Al_{0.35}(OH)_2](NTA^{3-})_{0.087}(NO_3^-)_{0.029}(CO_3^{2-})_{0.014}\cdot 0.41H_2O$. This formula takes into account the existence of NO_3 and CO_3 (FT-IR) and assumes that all the NTA exists in the trianion form.

FT-IR spectra of the NTA-LDH and (La,NTA)-LDH suggest (Fig. 1) that the content of NO_3 increases with incorporation of La and that NTA is still present within the LDH. We conclude, therefore, that in addition to La entering the interlayer NO_3 are also incorporated.

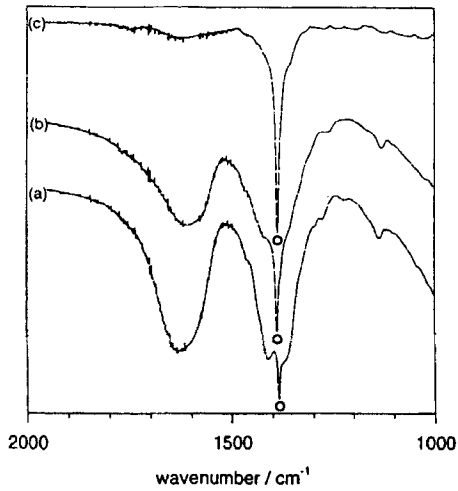

Fig. 1 FT-IR spectra of (a) NTA-LDH, (b) La, NTA)-LDH) and (c) a pure NO_3-containing LDH as reference. The bands marked O are for NO_3^-. The relative composition of NO_3 increases after reaction but NTA also remains present within the LDH.

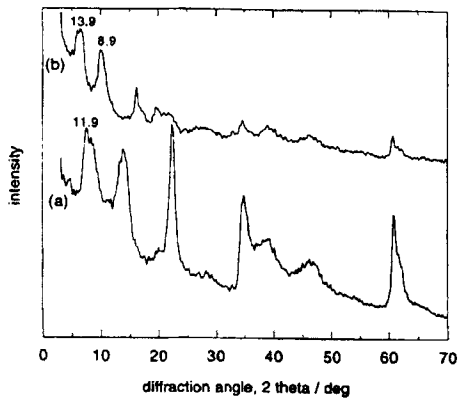

Fig. 2 Powder XRD patterns for (a) the NTA-LDH and (b) (La, NTA-LDH) (Corresponding d-values in Å are shown.) Phases with basal spacings of 13.9 and 8.9 Å are formed during complex formation within the interlayer.

The powder XRD patterns (Fig. 2) indicate that a phase with an increased basal spacing (~14 Å) is formed through the reaction of NTA-LDH and $La(NO_3)_3$. Additionally, however, a phase with basal spacing of 8.9 Å is also formed. The patterns suggest that a separate La hydroxide phase is not formed and that essentially all the La exists within the LDH phase.

Lanthanum and NTA are known to form 1:1 and 1:2 complexes and the structures of these complexes have been determined.[15-17] It is difficult, however, to predict from the FT-IR and powder XRD results in what form La exists within the interlayer. Although there is no direct evidence, it is reasonable to assume that La^{3+} is chelated by the NTA anions within the interlayer.

The fact that lanthanum and nitrate are simultaneously incorporated is rationalised as follows. The interlayer NTA anions chelate La with a consequential reduction in negative charge. As a result NO_3^- anions are incorporated to charge-balance. (La-NTA complexes are readily formed and are relatively stable (logK = 10.4, K =[La-NTA]/[La][NTA^{3-}])).[18] The increased basal spacing of the (La, NTA)-LDH results from the larger interlayer space volume required by the chelate complexes as well as additional nitrate anions.

We propose that the reaction may be ideally described by the following equations:

$$NTA^{3-}_{interlayer} + La(NO_3)_{3solution} \rightarrow [La\text{-}NTA]_{interlayer} + 3NO_3^-{}_{interlayer} \quad [1]$$

and/or

$$2NTA^{3-}_{interlayer} + La(NO_3)_{3solution} \rightarrow [La(NTA)_2]^{3-}_{interlayer} + 3NO_3^-{}_{interlayer} \quad [2]$$

In terms of stoichiometry the completion of [2] results in an ideal La/Al composition = 1/6, assuming that in the original NTA-LDH all the interlayer anion is in the trivalent form (i.e. NTA^{3-}).[14] Our experimental results, however, indicate that more La is incorporated (La/Al ~ 0.3). We conclude, therefore, that the reaction [1] also occurs. In this case, the resulting [La-NTA] remains intercalated, although in a neutral form.

Calcination of the (La, NTA) intercalated LDH

The powder XRD patterns of samples of the (La, NTA)-LDH calcined at various temperatures are shown in Fig. 3. The pattern of the sample calcined at 500 °C shows broad peaks at $2\theta \sim 42$ and 62 ° that are typical for a cubic Mg-Al mixed oxide.[1,2] The additional broad peak around $2\theta \sim 30$ ° is due to La oxide and hydroxide phases. The La oxide and hydroxide are clearer in the pattern for the sample calcined at 800 °C.[19,20]

In the pattern of the sample calcined at 1100 °C, reflections due to $LaAlO_3$[21] are dominant, with MgO[22] and $MgAl_2O_4$ (spinel)[23] also observed. Notably, La_2O_3 is not observed. The formation of spinel and MgO is usual following calcination of an LDH.[1,2] The absence of La_2O_3 is in contrast, however, with the pattern of the comparative solid-state reaction (Fig. 3(d)), in which La exists mainly as La_2O_3 and only in small part as $LaAlO_3$. We rationalise this difference in calcination behaviour by the fact that that in the mixed oxide formed at the beginning of the calcination of the LDH-complex the La that is present is well dispersed in the oxide matrix and in intimate contact with Al.

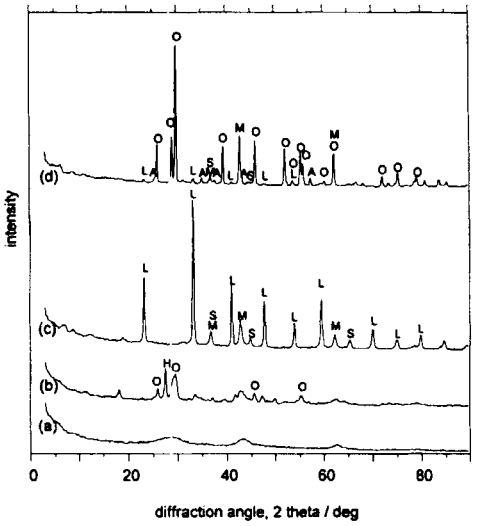

Fig. 3 Powder XRD patterns for the calcination products of (La, NTA)-LDH at (a) 500, (b) 800 and (c) 1100 °C and (d) the product of the comparative solid-state reaction. Reflections are marked for $LaAlO_3$ (L), La_2O_3 (O), $La(OH)_3$ (H), α-Al_2O_3 (A), MgO (M) and $MgAl_2O_4$ (S).

CONCLUSIONS

A pre-formed NTA-intercalated Mg-Al LDH reacts with lanthanum nitrate solution with the incorporation of La and NO_3^-. The driving force of the reaction is thought to be the formation of a chelate complex of La and NTA. When the resulting (La, NTA) intercalated Mg-Al LDH is calcined, $LaAlO_3$ is formed more effectively than by the conventional solid-state route. This is believed to occur because the La is well dispersed within the matrix.

ACKNOWLEDGMENT

The authors would like to thank Shin-Etsu Chemical Co. Ltd., for granting study leave to M. K and for providing ICP-AES analysis data.

References

[1] A. de Roy, C. Forano, K. El Malki and J.-P. Besse, in *Anionic Clays: Trends in Pillaring Chemistry, Synthesis of Microporous Materials* ed. M. L. Occelli and E. R. Robson, Van Nostrand Reinhold, New York, 1992; Vol. 2, p.108.

[2] F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today,* 1991, **11,** 173.

[3] S. P. Newman and W. Jones, *New J. Chem.*1998 **22,** 105.

[4] L. Ingram and H. F. W. Taylor, *Mineral. Mag.* 1967 **36,** 465.

[5] R. Allmann, *Acta Crystallogr., Sect. B*1968 **24,** 972.

[6] W. T. Reichle, *Solid State Ionics* 1986 **22,** 135.

[7] C. Barriga, J. M. Fernández, M. A. Ulibarri, F. M. Labajos and V. Rives, *J. Solid State Chem.* 1996 **124,** 205.

[8] V. Rives, F. M. Labajos, M. A. Ulibarri and P. Malet, *Inorg. Chem.* 1993 **32,** 5000.

[9] F. Basile, L. Basini, G. Fornasari, F. Gazzano, F. Trifirò and A. Vaccari, *J. Chem. Soc. Chem. Commun.* 1996, 2435.

[10] J. M. Fernández, C. Berriga, M. A. Ulibarri, F. M. Labajos and V. Rives, *Chem. Mater.* 1997 **9,** 312.

[11] 1 S. Miyata and T. Hirose, *Clays Clay Miner.* 1978 **26,** 447.

[12] E. P. Giannelis, D. G. Nocera and T. J. Pinnavaia, *Inorg. Chem.*1987 **26,** 203.

[13] K. A. Carrado, J. E. Forman, R. E. Botto and R. E. Winans, *Chem. Mater.* 1993 **5,** 472.

[14] M. Kaneyoshi and W. Jones, *J. Mat. Chem.* 1999 **9,** 805.

[15] K. W. Bagnall, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two* 1975 **7,** 41.

[16] L. L. Martin and R. A. Jacobson, *Inorg. Chem.* 1972 **11,** 2785.

[17] R. Starynowicz, *Acta Cryst.* 1987 **C43,** 1509.

[18] In *Bunseki Kagaku Databook* ed. Nippon Bunseki Kagaku-kai, Maruzen Co. Ltd., Tokyo; 1993, 91.

[19] JCPDS-ICDD *PDF Database* 1998 No.83–1355.

[20] JCPDS-ICDD *PDF Database* 1998 No.83–2034.

[21] JCPDS-ICDD *PDF Database* 1998 No.31–0022.

[22] JCPDS-ICDD *PDF Database* 1998 No.45–0946.

[23] JCPDS-ICDD *PDF Database* 1998 No.21–1152.