Comment on “Direct Observation of a Metastable Solid Phase of Mg/Al/CO_3-Layered Double Hydroxide by Means of High-Temperature in Situ Powder XRD and DTA/TG”[1]

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Kanezaki has recently reported[1] the formation of a metastable phase in the temperature range 180−380 °C during calcination in air of Mg,Al-carbonate layered double hydroxides (LDHs). The results reported by this author, obtained by in situ HTXRD, are important, as most of the studies reported in the literature on calcined LDH’s are carried out at room temperature, where the state of the sample may have changed during cooling, exposure to atmosphere, and handling.

According to Kanezaki, from room temperature to ca. 180−200 °C the layered structure (Phase I), with interlayer water molecules and carbonate anions, is stable, with a basal spacing of 7.8 Å. Crystallization of MgO is observed above 400 °C, and $MgAl_2O_4$ appears near 1000 °C. Between both temperatures (i.e., 200−400 °C) a metastable phase (Phase II), characterized by a basal spacing of 6.6 Å, is observed. TG results show two weight losses extending between ca. 25−220 and 300−450 °C, the first one ascribed to removal of unreacting interlayer water molecules and through reaction with interlayer carbonate anions (which are removed as CO_2) according to:

$$CO_3^{2-} + H_2O \rightarrow CO_2(g) + 2OH^-$$

(i.e., the interlayer anion balancing the positive charge in excess in the brucite-like layers of the metastable Phase II would be hydroxyl groups). The second weight loss corresponds to removal of hydroxyl groups as water molecules.

Kanezaki concludes that Phase II is also a layered material but is one that contains interlayer hydroxyl groups; the “less bulky” nature of the interlayer hydroxyl anion compared to the carbonate would explain the reduction of the interlayer distance in the XRD patterns from 3.0 Å (Phase I) to 1.8 Å (Phase II), these values being calculated from the measured basal spacings (7.8 and 6.6 Å, respectively) and assuming 4.8 Å for the thickness of one layer of Mg/Al-double hydroxide.[2]

This conclusion is rather surprising if the sizes of these species are considered. The basal spacing of Phase I is in agreement with location of the interlayer carbonate anions with their molecular planes parallel to the internal surface of the layer,[3,4] the width of the carbonate being 3.0 Å, and this value coinciding with twice the van der Waals radius of the oxygen atom.[5] However, the ionic radius of hydroxyl is 1.19−1.23 Å (depending on the coordination number),[5] and thus the interlayer distance in a LDH containing exclusively hydroxyl groups in the interlayer space would be 2.38−2.46 Å, a value markedly larger than that found in Phase II (1.8 Å), attributed by Kanezaki to the presence of this species. Moreover, we should expect that if the carbonate anion is located with its plane parallel to the layers, its thickness would approximately correspond to that of a single oxygen atom, i.e., the same as that of a hydroxyl group. Thus, no significant difference would be expected between the interlayer space of a sample with carbonate or with hydroxyl. Also, the spacing would be also the same for interlayered bicarbonate species, HCO_3^-, which formation has been claimed in some cases, because of pH lowering during washing of the samples[3] ($CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$).

Contrary to what Kanezake states,[1] a LDH with interlayer hydroxyl anion has been reported in the literature: it is meixnerite, with a formula $Mg_6Al_2(OH)_{18}\cdot 4H_2O$, i.e., $[Mg_{0.75}Al_{0.25}(OH)_2](OH)_{0.25}\cdot 0.5H_2O$, and a basal spacing of 7.64 Å, corresponding to a thickness for the interlayer of 2.84 Å.[3] This value is only 2% smaller than that the hydrotalcite (Phase I) synthesized by Kanezaki containing interlayer carbonate. It should be, however, pointed out that meixnerite contains also interlayer water molecules, while these should have been removed in the high-temperature cell used by Kanezaki.

We have previously reported on the evolution of Mg,Al-carbonate LDHs during calcination.[6−8] Decomposition takes place in two steps, as reported by Kanezaki, but mass spectrometry analysis of gases evolved during calcination (Figure 1) indicates that during the first decomposition step, almost exclusively water (*m*/*e* 18, H_2O^+) is evolved, the observed small amount of carbon dioxide (*m*/*e* 44, CO_2^+) coming probably from CO_2 adsorbed on the external surface of the particles, which are known to be highly basic; for the second weight loss, only significant amounts of both CO_2 and H_2O are found in the gases evolved, and so decomposition can be summarized as consisting of a first step, corresponding to removal of interlayer water molecules, and a second step, due to removal of interlayer carbonate as CO_2 and of layer hydroxyls as H_2O. Weight loss quantification during thermal decomposition of our samples are in agreement with these two decomposition steps.

Approximate quantification of the amount of water evolved in the two steps indicate a ratio close to 0.45 (first peak:second peak), in agreement with the expected value (0.52) from the chemical formula of the hydrotalcite used.

Recently, López et al.[9] have reported a similar thermal decomposition pattern for hydrotalcites prepared by sol−gel techniques: removal of interlayer water up to 250 °C, dehydration and decarbonation, leaving a Mg,Al oxohydroxide up to 450 °C, and finally decomposition to the solids ($MgAl_2O_4$ and MgO) up to 900 °C.

Thermogravimetric analysis does not either provide a conclusive answer about the decomposition process. From the weight loss corresponding to the first decomposition step, the amount of interlayer water can be calculated, whichever the decomposition path assumed, taking into account that after

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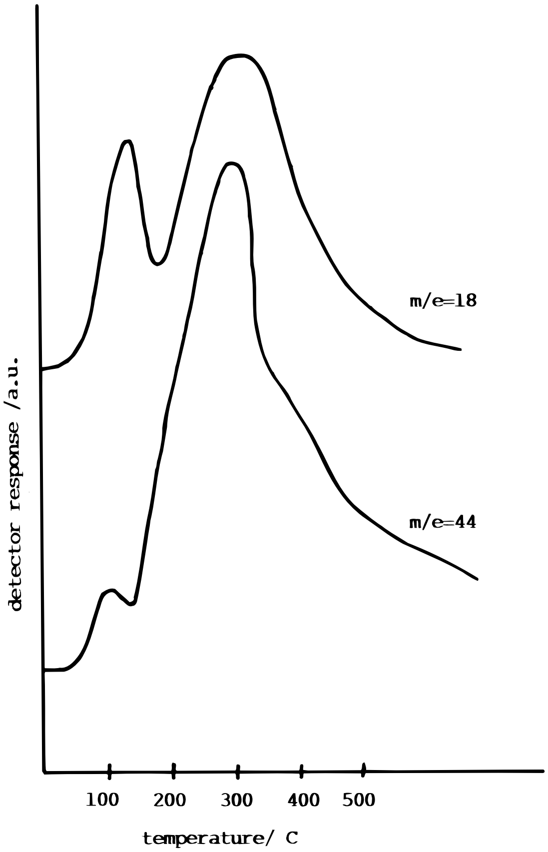

Figure 1. Mass spectrometry analysis of gases evolved during thermal decomposition of a Mg,Al-carbonate layered double hydroxide (heating rate 10 °C/min).

calcination at 900−1000 °C, the corresponding oxides are formed. We have calculated the amount of interlayer water for four hydrotalcites with different Mg/Al ratios.[10] The values obtained assuming Kanezaki's decomposition path were 0.58, 0.39, 0.33, and 0.37 H_2O/formula, while assuming that only interlayer water is removed in the first decomposition step, the values were 0.88, 0.66, 0.57, and 0.61, respectively. These values are markedly different, following one method or another, but, unfortunately, no confirmation can be reached about their validity from the second weight loss, leading to formation of the corresponding oxides, as assuming one formula or another (i.e., that with water content calculated assuming Kanezaki's decompositon or the other), the expected weight losses after the second decomposition step are coincident within experimental error.

Alternatively, if bicarbonate species are formed in Phase I from carbonate because of pH lowering during washing of the samples until total removal of chloride (existing from the starting chemicals used for synthesis), the spacing would coincide with that of carbonate and, upon calcination at 250 °C, the weight loss calculated roughly coincides with the experimental value. Nevertheless, the origin of the so small spacing for Phase II remains still obscure.

Upon calcination of LDH's containing other interlayer anions, the decrease observed in the interlayer spacing has been explained by other authors on the basis of grafting of the interlayer anions to the brucite-like layers.[11] However, the observed decrease in spacing and simultaneous removal of any carbon anion can only be explained assuming that during the first weight loss, some hydroxyl groups from the brucite-like layers are converted to oxide ions:

$$CO_3^{2-} + 2OH^- \rightarrow CO_2(g) + H_2O\ (g) + 2O^{2-}$$

In such a case, removal of all interlayer species would leave the brucite-like layers only appart because of electrostatic repulsion, and the weight loss calculated roughly matches the experimental value recorded. To confirm this point, however, in situ FT-IR analysis of the original and the calcined samples (Phases I and II) would be desirable to confirm the nature of the interlayer anion; unfortunately, we do not have currently access to this technique.

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