

A study of structural memory effects in synthetic hydrotalcites using Environmental SEM

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Abstract

The 'memory' effect in synthetic hydrotalcite was demonstrated using d(001) and d(002) peaks in XRD patterns. These peaks were present in the hydrotalcite before it was calcined, and after it was reformed, but not in the thermally activated hydrotalcite. SEM images were taken of the hydrotalcite, to show the layering and size of the crystals. Environmental SEM (ESEM) images were taken of the thermally activated hydrotalcite, and then manipulation of temperature and pressure allowed water to condense on the sample. The ESEM images show that the layered structure is reforming following exposure to water.

Keywords: *Hydrotalcites; Structural memory effects; Environmental SEM; X-ray diffraction;*

1.0 Introduction

In recent years, increasing levels of research has been invested in discovering new 'smart materials' [1]. Traditionally, the resulting properties of a material would tell what function the material might have. Now the focus is on designer materials which are made for specific functions [1]. Smart materials can be made so they will respond with a significant change in properties when subjected to environmental changes, such as temperature, pH, chemicals or light [2].

Smart materials can be designed to have a memory effect, which can be a light memory [3-5], or a structural memory [6-8]. The type of memory demonstrated by hydrotalcites is a structural memory. Hydrotalcites are based on the brucite structure, $Mg(OH)_2$ [9-11], where a trivalent cation substitutes for some of the divalent cations, which results in a positive layer charge. This positive layer charge is balanced by the incorporation of an anion. The resulting mineral has layers of ordered cations between hydroxyl sheets,

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giving hydrotalcites the acronym ‘double layer hydroxides.’ As there is no overall charge, hydrotalcites are quite stable. Many types of hydrotalcites can be formed from different combinations of divalent and trivalent cations, and different interlayer anions. The anion may be divalent, such as carbonate, sulphate and phosphate, or it may be monovalent, such as chloride or nitrate. Hydrotalcites generally prefer to have a divalent anion in their structure. Studies have been done on the preference of hydrotalcites to anions, and a divalent anion will usually out-compete the monovalent anion [12-14]. These studies also demonstrated that hydrotalcites have a strong preference to the carbonate anion.

The interesting properties of hydrotalcites arise when they are calcined; this process removes the interlayer water, interlayer anions, and the hydroxyls. The resulting material is an atomic mixture of metal oxides. The structure is directly related to the arrangement of the metals in the hydrotalcite and could not be achieved by mechanical means.

The exact calcination temperature will vary depending on the type of hydrotalcite used, but is usually between 573-773K [8]. The calcination effectively destroys the hydrotalcite structure. The calcined hydrotalcite is able to reform the original structure when it is exposed to water and anions [8]. Water will be absorbed to reform the hydroxyl layers; anions and water will be absorbed into the interlayer. The anions that will be absorbed do not necessarily need to be the anion that was in the original hydrotalcite, any available anion will be absorbed [12]. The ability to remove anions is what makes the ‘memory effect’ of hydrotalcites so useful. They can be used effectively to remove harmful anions; both organic [12, 15] and inorganic [16] from a solution. The ‘memory effect’ also has many catalytic applications [17, 18].

2.0 Experimental

Synthetic hydrotalcite $Zn_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ was prepared by the urea method [9]. A solution was prepared containing 0.165M Al^{3+} (as $AlCl_3 \cdot 6H_2O$) and 0.335M Zn^{2+} (as $ZnCl_2 \cdot 6H_2O$). To this solution, 1.65M of urea ($CO(NH_2)_2$) was added, and dissolved. The solution was heated to 363K for 24 hours, then filtered and washed several times. The composition of the hydrotalcites was checked by electron probe analyses. The phase composition was checked by X-ray diffraction. SEM and Environmental SEM imaging was carried out using an FEI Quanta 200 ESEM, which was fitted with a Peltier-cooled stage during ESEM operation.

The calcined hydrotalcite (C-HT) was prepared by heating a sample in a furnace at 573K for 1 hour. The reformed hydrotalcite (R-HT) was prepared for XRD by stirring the C-HT in a dilute carbonate solution for 2 hours.

3.0 Results and Discussion

3.1 X-ray diffraction

X-ray diffraction patterns of the synthetic hydrotalcites are shown in Fig. 1a. Before calcination, the hydrotalcite (HT) clearly has a layered structure. The most intense peak of the HT is actually 3 peaks very close together, and is shown expanded in Fig. 1b.

This gives a d(001) spacing of 7.81-7.61Å, which corresponds to the distance between the hydroxyl layers. Similarly, three peaks at 3.92-3.81Å were present, which is attributed to the d(002) peak. The three d(001) and d(002) peaks potentially indicate the presence of hydrotalcites with three interlayer spacings. A possible explanation is there are three different arrangements of the anion between the layers, such as the anion laying flat on the surface, perpendicular to the surface, or somewhere in between. As this hydrotalcite was synthesised at a relatively high temperature (363K), the energy from heating could allow the anion to exist in other arrangements.

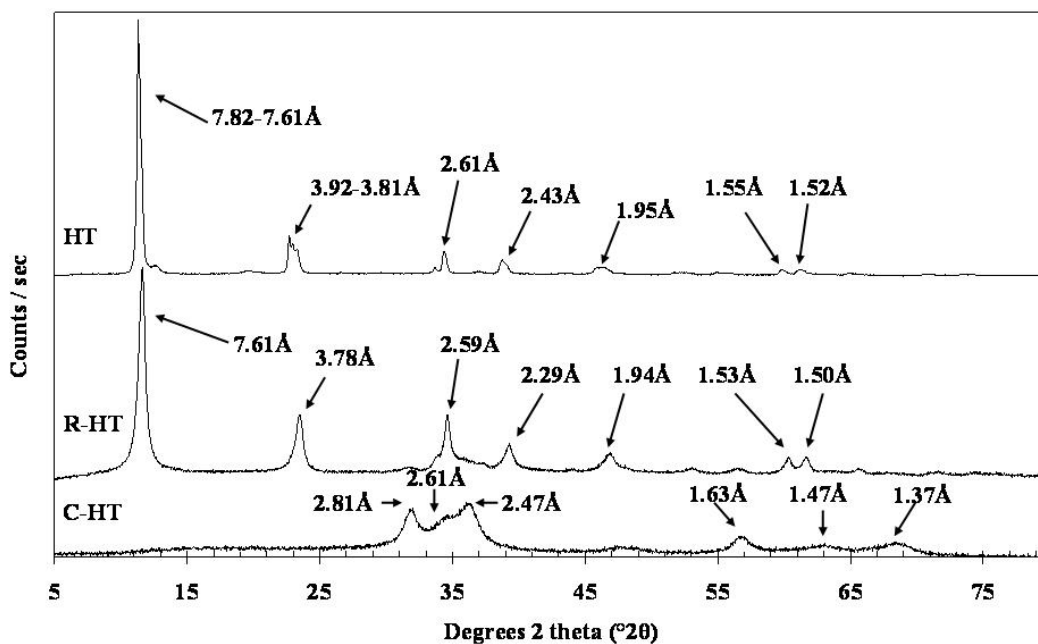


Figure 1a

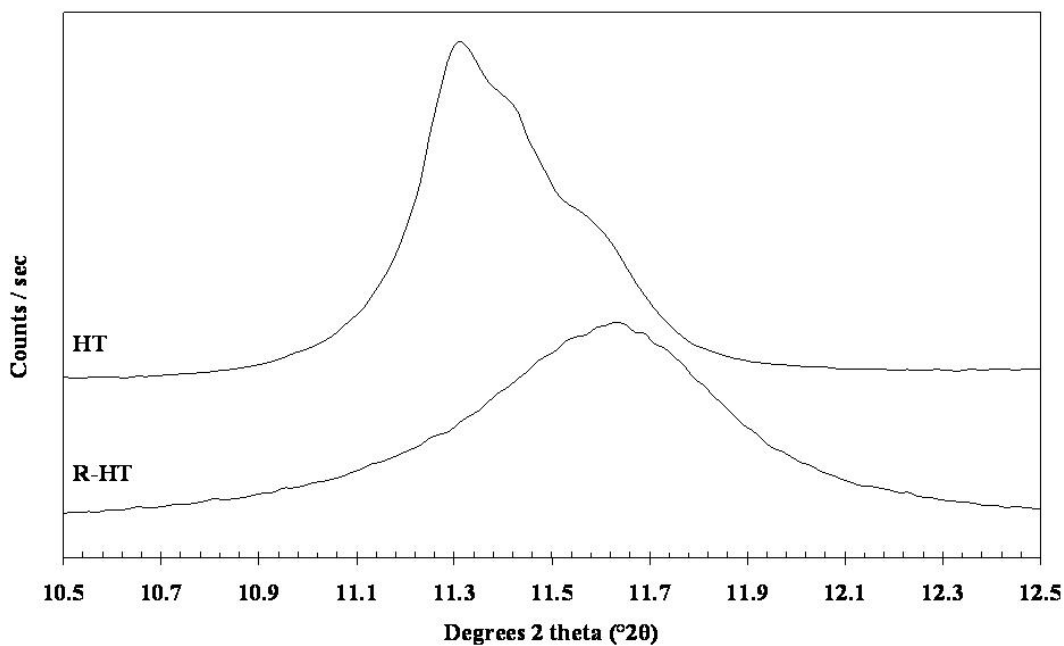


Figure 1b

The XRD pattern of the C-HT shows that the layered structure has been destroyed as the d(001) and d(002) peaks are not present. There is some structure which exists, but the increase in baseline shows overall, the C-HT is quite disordered.

The R-HT pattern shows that the layered structure has been restored due to the presence of the d(001) and d(002) peaks. However, there is no longer 3 peaks close together, which shows that there is now only one hydrotalcite interlayer spacing present; and only one anion arrangement. This causes a shift of 0.01-0.02 Å of the other hydrotalcite peaks. The reformation of the hydrotalcite was done at room temperature, which perhaps was not of sufficient energy to allow the different anion arrangements.

The XRD patterns show that when the synthetic hydrotalcite is thermally activated, the layered structure is destroyed. The layered structure can be restored if the thermally activated hydrotalcite is exposed to water and carbonate. The restoration of the layered structure in hydrotalcites is the 'structural memory effect'.

3.2 SEM and Environmental SEM

Fig. 2 is a high vacuum SEM image of gold coated synthetic hydrotalcite, which shows the layered hydrotalcite sheets. The image demonstrates the crystals are very thin, as some appear semitransparent due to electron beam penetration through the crystal. Considerable variation in the crystal size was detected, ranging from about 1 µm to 5 µm. The crystals appear very flat, and some are broken. Some of the layered crystals can be seen transversely, allowing an estimate of the thickness as about 0.3 µm. Using the d(001) value obtained from the XRD results, one sheet would be made up of about 400 layers.

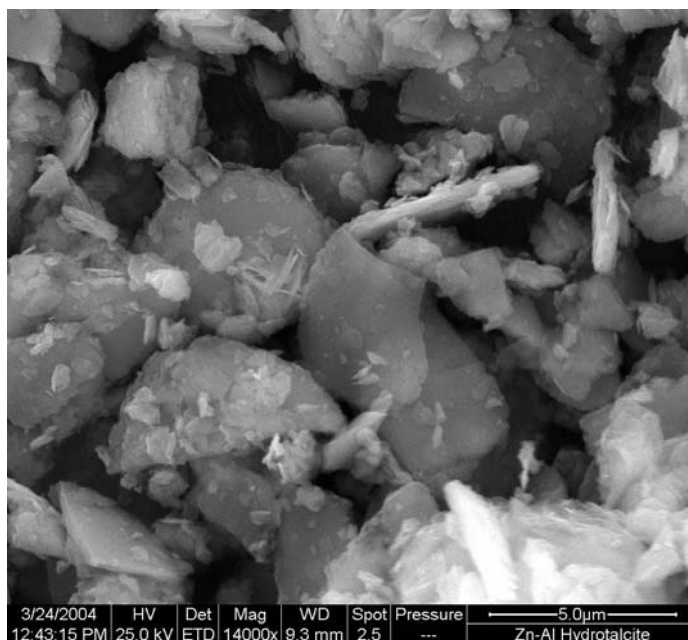


Figure 2

An ESEM image of the calcined hydrotalcite taken at 3 Torr (0.4 kPa) chamber pressure is shown in **Fig. 3**. ESEM does not require a conductive coating; hence the contrast of the image is low, attributed to scattering of the electron beam in the specimen chamber

gas (water vapour). The structure is still crystalline, and the crystals have a tendency to cluster together; though not in layers. There are two clusters of crystals present in this image, as well as some individual crystals of different sizes.

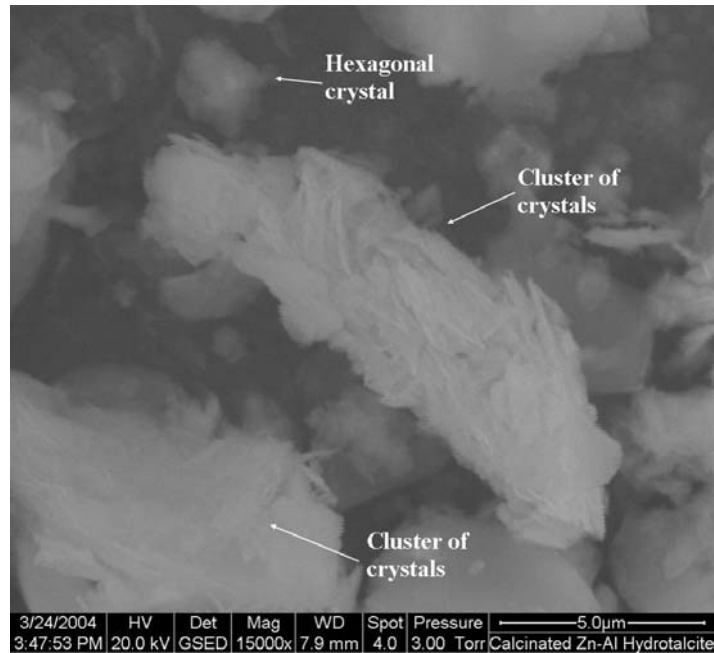


Figure 3

The second ESEM image, shown in **Fig. 4**, was taken after manipulation of specimen temperature and pressure conditions inside the chamber, and is of the same area as **Fig. 3**. An increase in pressure and decrease in temperature allowed water vapour to condense on the sample. The sample was left for about 10 minutes under these conditions, before the temperature was increased and the pressure decreased to evaporate the condensed water. The contrast of this second image is better, probably as a result of increased electrical conductance following absorption of water. The cluster of crystals that was located in the bottom left corner of **Fig. 3** has broken up, and is starting to form layers, but the second cluster has not yet started to break up. A hexagonal crystal at the top of the image has increased in size, from 2.5 to 2.8 µm, suggesting that it has absorbed some water.



Figure 4

What was observed was not a complete reformation of the layered structure, as the low temperatures required for water condensation (about 276K) meant that the reaction is not kinetically favoured, and it would require a long period of time for this reaction to complete under these conditions. However the reaction had proceeded far enough that the beginnings of the structural memory effect could be observed.

4.0 Conclusion

Using XRD combined with SEM and ESEM, the structural changes that occur in hydrotalcites during calcination were studied. The XRD patterns showed that hydrotalcites are able to reform a layered structure, and also showed that there were three types of anion arrangements present in the hydrotalcite. After thermal activation, and reforming the hydrotalcite, there was only one anion arrangement. The advantage of using ESEM is that it allows images of the hydrotalcite to be taken while the reaction is occurring without removing the sample, and it is possible to measure accurately the changes in size of particular crystals.

5.0 Acknowledgements

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