

Thermal decomposition of Co–Al layered double hydroxide: Identification of precursor to oxide with spinel structure

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Abstract. The layered double hydroxide (LDH) of Co with Al decomposes to yield an oxide residue with the spinel structure below 250°C. The decomposition reaction is preceded by the formation of an intermediate hydroxide in which the metal hydroxide layers are regularly stacked about the *c*-crystallographic axis, but the layers themselves are aperiodic. Aperiodicity is modeled by locating randomly chosen Co²⁺ ions in tetrahedral sites in the interlayer region. This phase is characterized by a single strong basal reflection in its powder diffraction pattern. All other reflections are extinguished on account of (i) turbostratic disorder which destroys all *hkl* reflections and (ii) layer aperiodicity, which destroys all two dimensional *hk* reflections. Given its topochemical relationship with the spinel structure, such an intermediate is a necessary precursor to spinel formation.

Keywords. Layered double hydroxide; thermal decomposition; topochemical relationship.

1. Introduction

Layered double hydroxides (LDHs) are mixed metal hydroxides having the general formula, [M(II)_{1-x}M'(III)_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·mH₂O, where M(II) = Mg, Ca, Fe, Co, Ni, Cu, Zn and M'(III) = Al, Cr, Fe, Co (Williams and O'Hare 2006). Among the anions, Aⁿ⁻, the most ubiquitous in naturally occurring LDHs is the CO₃²⁻ anion (Duan and Evans 2006). All the cations in LDHs occupy octahedral sites. The LDHs decompose below 500°C to yield an oxide residue. Following the work of the late Professor Figlarz (Figlarz *et al* 1990), the decomposition of the LDH is expected to take place topotactically. Consequently, the Mg–Al LDH immediately on decomposition yields a defect oxide, Mg_{1-x}Al_{2x/3} O_{x/3}, with the rock salt structure (Sato *et al* 1986). The cations remain in their octahedral sites in the oxide. The defect rocksalt is, however, metastable and transforms to a mixture of periclase MgO and spinel MgAl₂O₄ on sintering at temperatures above 1000°C (Rey *et al* 1992). In contrast with this observation, the LDH of Co with Al decomposes below 300°C to directly yield the spinel oxide (Perez-Ramirez *et al* 2001). Kannan and Swamy (1999) attributed the formation of the spinel around 200°C to the facile oxidation of Co²⁺ to Co³⁺ and the thermodynamic stability of

the spinel compared to CoO in air. If this transformation were to occur topotactically, the formation of the spinel must involve the diffusion of the Co²⁺ ions from the octahedral sites in the precursor LDH to the tetrahedral sites of the oxide. However, the exact mechanism of the transformation of Co–Al LDH to spinel is not known. In this paper, we study the thermal decomposition of the Co–Al–CO₃²⁻ LDH by *in situ* variable temperature powder X-ray diffraction (VTPXRD), and follow the structural changes taking place in the LDH prior to the decomposition reaction. We report the formation of a precursor hydroxide phase having a topochemical relationship with the spinel structure.

2. Experimental

2.1 Synthesis

Co–Al–CO₃²⁻ LDH was prepared by homogeneous precipitation by the hydrolysis of urea (Costantino *et al* 1998). Solid urea was added to 40 ml of a 0.5 M mixed metal [Co(II) + Al(III)] nitrate solution maintaining the urea/[Co(II) + Al(III)] molar ratio at 3.3. The clear solution obtained was hydrothermally treated at 140°C for 24 h in a teflon lined autoclave under autogenous pressure (50% filling). The solids were recovered by filtration, copiously washed to constant pH and then dried at 80°C.

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2.2 Characterization

In situ variable temperature powder X-ray diffraction (VTPXRD) was carried out on a Philips X'pert MPD system (graphite secondary monochromator) connected to an Anton-Paar high temperature XRK assembly using $\text{CuK}\alpha$ ($\lambda = 1.541 \text{ \AA}$) radiation. The sample was mounted in a high temperature cell and heated at 5°C min^{-1} in steps of 25°C and stabilized for 10 min before measurements. The operating voltage and current were 40 kV and 40 mA, respectively. The step size was $0.05^\circ 2\theta$ with a step time of 1 s.

Thermogravimetric studies were carried out in a Mettler Toledo TGA/SDTA 851^e, Star^e 7.01 system. The sample was heated to 100°C and held at this temperature for 30 min to expel adsorbed water and then ramped up to 800°C (heating rate 5°C min^{-1} , flowing air).

2.3 DIFFaX simulation

The structural changes taking place in the LDH during heating were examined by DIFFaX simulation studies (Version 1.807) (Treacy *et al* 1991). The background was subtracted from all the PXRD patterns prior to simulation by fitting a twelve coefficient polynomial. The details of DIFFaX simulation studies for carbonate LDHs are given in our earlier papers (Thomas *et al* 2004; Radha *et al* 2005, 2007a). The structure of the Co–Al LDH obtained by Rietveld refinement (Space group $R\text{-}3m$; $a = 3.066 \text{ \AA}$, $c = 22.593 \text{ \AA}$) was used to define the metal hydroxide layer (AC) together with the interlayer atoms.

3. Results and discussion

In an earlier paper (Radha *et al* 2007b), we reported the refinement of the Co–Al– CO_3^{2-} LDH structure by Rietveld method. The structure belongs to the $R\text{-}3m$ space group with Co^{2+} and Al^{3+} cations randomly distributed in octahedral sites formed by the hexagonal close packing of hydroxyl ions. The metal hydroxide slab is similar to that observed in mineral brucite, $\text{Mg}(\text{OH})_2$, except that it is positively charged due to the presence of Al^{3+} ions. An interlayer with carbonate anions and water molecules balances this charge and gives overall stability to the LDH through ionic and H-bonding with the brucite-like layers. This corresponds to the orientation of the planar carbonate anions parallel to the metal hydroxide layer at the centre of the interlayer region. This structure comprises a triple layered cell ($a = 3.066 \text{ \AA}$; $c = 22.593 \text{ \AA}$) with the metal hydroxide layer stacking sequence $AC\ CB\ BA\ AC\ \dots$, corresponding to the $3R_1$ polytype. A polytype of comparable stability, $2H_1$, has the stacking sequence $AC\ CA\ AC\ CA\ \dots$.

Figure 1 shows the *in situ* VTPXRD patterns of the Co–Al– CO_3^{2-} LDH recorded at different temperatures in

air. The following changes take place in the PXRD patterns on heating the LDH:

(I) The intensity of the basal 006 reflection ($2\theta \sim 23^\circ$) relative to the 003 ($2\theta \sim 11.5^\circ$) progressively decreases with increase in temperature up to 175°C . At 200°C , the 006 reflection is completely extinguished.

(II) Although the peaks in the mid- 2θ region retain the features of the $3R_1$ polytype, they are progressively non-uniformly broadened on heating from $50\text{--}175^\circ\text{C}$.

(III) The high angle reflections remain unaffected up to 125°C and above this temperature begin to show asymmetric broadening with a decrease in the relative intensity.

(IV) At 200°C , the PXRD pattern shows a single reflection at $13.5^\circ 2\theta$. All other reflections are extinguished. This reflection corresponds to a basal spacing of 6.6 \AA less than that in the as-prepared LDH (7.5 \AA).

(V) At 225°C , all the reflections are extinguished indicating a total disintegration of the structure and the generation of an X-ray amorphous residue.

(VI) The pattern at 275°C shows the emergence of a broad reflection at $37^\circ 2\theta$, corresponding to the 311 reflection of the spinel phase.

Further evidence for the collapse of hydroxide structure can be seen in TGA (figure 2). The TGA curve of the Co–Al LDH in air shows a net mass loss (29.2%) whose

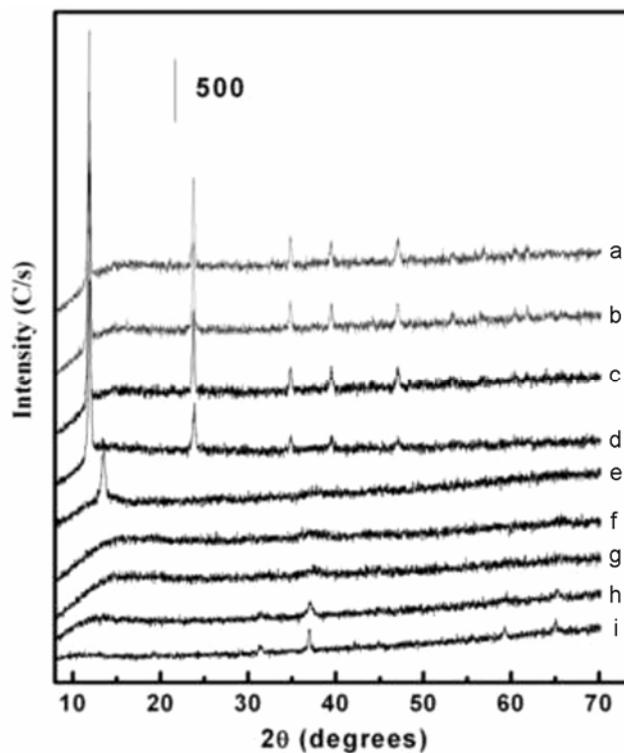


Figure 1. *In situ* variable temperature PXRD patterns of the Co–Al– CO_3^{2-} LDH calcined in air at different temperatures ($^\circ\text{C}$) (a) 50, (b) 125, (c) 150, (d) 175, (e) 200, (f) 225, (g) 275, (h) 600 and (i) 800.

major thermal transformation is complete around 275°C. The DTG curve shows two closely spaced points of inflection at 220–250°C corresponding to the near simultaneous dehydration and decomposition reactions of the LDH. The PXRD pattern of the resulting oxide residue at 800°C could be indexed to a spinel phase (figure 3). In this phase, the cations are distributed in both octahedral and tetrahedral sites.

What is of interest in the current study is the exact mechanism of formation of the spinel structure starting from the LDH. For this we examine in detail the structural changes taking place in the LDH prior to the decomposition using DIFFaX simulations of the PXRD patterns obtained during the thermal treatment of LDH.

The non-uniform broadening of different reflections and a variation in their relative intensities in the PXRD

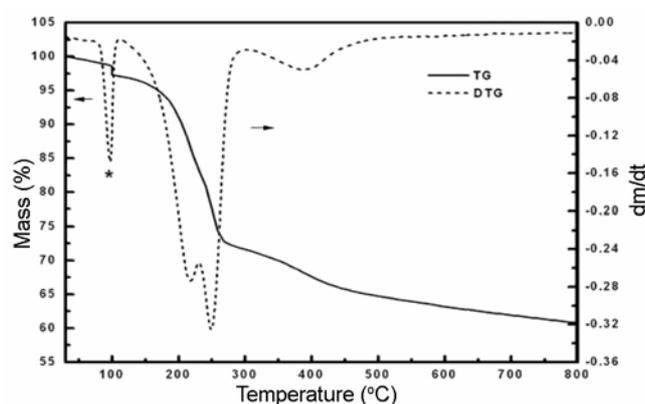


Figure 2. TG–DTG curve of the as prepared Co–Al–CO₃²⁻ LDH in air. The feature marked by the asterisk in the DTG is on account of the stay at 100°C.

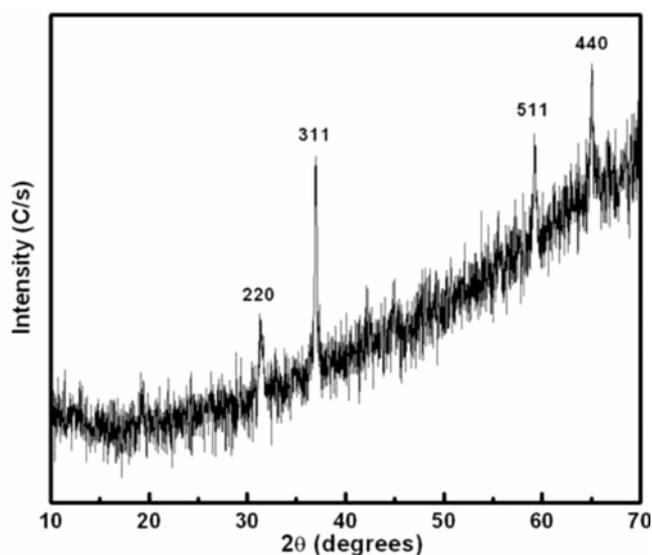


Figure 3. PXRD pattern of the oxide residue obtained from the Co–Al–CO₃²⁻ LDH at 800°C.

patterns is on account of structural disorder. We list below the effect of different types of structural disorder on the PXRD patterns of the LDHs.

(I) The intensity of the 006 reflection is proportional to the electron density of the interlayer (Thomas *et al* 2004, 2006). Loss of intercalated water on heating lowers the electron density in this region and progressively diminishes the intensity of the 006 reflection relative to the 003 reflection from 34% when the interlayer is full to 15% when the interlayer region is dehydrated.

(II) The presence of stacking faults and turbostraticity affects the mid- 2θ region and produces non-uniform broadening of $h0l/0kl$ reflections (Radha *et al* 2005; Thomas and Kamath 2006). The stacking faults arise due to intergrowth of different polytypes.

(III) Turbostratic disorder arises due to the random orientation of successive layers about the stacking direction. The asymmetric broadening of the high angle 113 reflection is characteristic of turbostratic disorder (Warren and Bodenstern 1966; Hines *et al* 1997).

Using this information we simulate the VTPXRD patterns shown in figure 1. The as-prepared LDHs are known to incorporate stacking faults arising out of the random intergrowths of the $3R_1$ and $2H_1$ polytypes. Figure 4a shows the simulated PXRD pattern for the Co–Al LDH obtained at 50°C (figure 1a). Incorporation of 12% $2H_1$ motifs in $3R_1$ polytype produced the required broadening in the mid- 2θ region of the simulated pattern.

Heating this sample to 150°C caused further broadening of the mid- 2θ reflections along with decrease in the intensity of the 006 peak and asymmetric broadening of (11) reflection (figure 1c). A matching simulation of this pattern (figure 4b) was realized by incorporating 30% turbostratic disorder in the $3R_1$ polytype. While simulating this pattern (figure 4b), the O content of the interlayer was also decreased from 1.14–1.02 to reflect the loss of water on dehydration. This resulted in a good fit of the relative intensity of the 006 reflection. The PXRD pattern obtained at 175°C (figure 1d) shows a broadening of all the reflections and this pattern could be simulated by introducing 50% turbostratic disorder in the $3R_1$ polytype. The O content in the interlayer was further reduced to 0.72 indicating further dehydration of the sample (figure 4c).

Figure 1e shows the PXRD pattern of Co–Al LDH at 200°C. Such a pattern in which all the reflections are extinguished except for the solitary basal reflection at $13.5^\circ 2\theta$ (6.6 Å) has hitherto not been reported. This is an exact inverse of the pattern observed for cationic clays with the so-called ‘house of cards’ structure (Pinnavaia *et al* 1984). In the latter, progressively truncated layers are stacked resulting in a tapering of electron density along the stacking direction. Such a construction of TOT layers destroys the periodicity in the electron density along the stacking direction. Consequently, the PXRD pattern shows extinction of the basal $00l$ reflections leaving the other reflections unaffected.

The PXRD pattern in figure 1e is indicative of a situation in which, the periodicity of the electron density is conserved along the stacking direction, also the *c*-crystallographic axis. However, each layer is distorted leading to the loss of periodicity in the electron density within the layers. Such a structure is expected to give a PXRD pattern having only basal reflections as observed in figure 1e.

The question now arises as to how the metal hydroxide layer can be distorted. The movement of a fraction of cations away from the octahedral sites of brucite-like hydroxide layers into the interlayer tetrahedral sites can lead to such an irregularly distorted metal hydroxide layer. Such a model is chemically feasible as Co^{2+} ions are known to be distributed in octahedral and tetrahedral sites in the basic salts of Co as well as in the α -modification of cobalt hydroxide. The latter has a composition $[\text{Co}_{0.825}^{\text{octa}}\text{Co}_{0.348}^{\text{tetra}}(\text{OH})_2]^{0.348+}\text{Cl}_{0.348}\cdot 0.456\text{H}_2\text{O}$ (Ma et al 2006).

To simulate this hydroxide phase we generated a metal hydroxide layer by making appropriate changes in the model structure of the precursor Co–Al– CO_3^{2-} LDH. Half the Co^{2+} ions were randomly placed in interlayer tetrahedral sites formed by three O atoms of the metal hydroxide layers acting as base and an interlayer O being the apex. These sites ($x, -x, 0.25$) are located exactly above the 18*h* sites ($x, -x, 0.5$) ($x = 0.1063$) of the interlayer O atoms. The site symmetries of the interlayer atoms are essentially retained as such. Such a migration of the Co^{2+} ions results in an aperiodic metal hydroxide layer. These aperiodic layers are, however, stacked regularly, but with a random orientation about the stacking direction. Such a stacking yields a periodic electron density along the

stacking direction, while at the same time the random orientation of the layers about the stacking direction results in turbostratic disorder.

Figure 5 gives the DIFFaX simulation of the PXRD pattern reported in figure 1e and is obtained for a turbostratically disordered stacking of aperiodic hydroxide layers. The pattern was simulated for the fully dehydrated phase (interlayer O content is 0.5, corresponding only to the intercalated CO_3^{2-}). The simulated pattern shows that the introduction of aperiodicity in the hydroxide layers substantially destroys the intensity of the reflections in the mid and higher angle regions ($> 30^\circ 2\theta$). The observed pattern is a limiting case, in which all reflections, except for the basal reflection, are extinguished. A brief summary of all DIFFaX simulations is given in table 1.

In carbonate LDHs, crystal chemical and thermodynamic considerations direct the carbonate anions to trigonal prismatic interlayer sites. These are crystallographically well-defined sites for the C and O atoms of the CO_3^{2-} ions and facilitate hydrogen bonding between the oxygen atoms of the carbonate ions and the hydroxyl ions of the layer. The carbonate LDHs crystallize either in $3R_1$ or in the $2H_1$ polytype or as an intergrowth of these two polytypes as all of them have purely prismatic interlayer sites. The precursor Co–Al LDH prepared by the urea hydrolysis method crystallizes in $3R_1$ polytype. Heating of the Co–Al LDH increases the overall thermal energy of the system and this energy is expected to add to the entropy of the system. Stacking disorders do not affect the enthalpy of the system but impart thermodynamic stability to the structure through the entropy contribution (Verma and Krishna 1966). Among these disorders, stacking faults with $3R_1$ and $2H_1$ motifs having purely prismatic interlayer sites further conserve the strength of the hydrogen bonding and are favoured at low

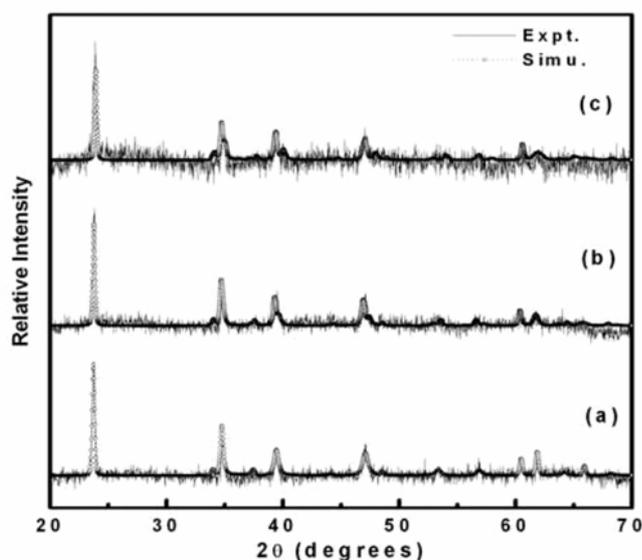


Figure 4. DIFFaX simulated PXRD patterns of the Co–Al– CO_3^{2-} LDH overlaid with the corresponding experimental patterns at (a) 50°C, (b) 150°C and (c) 175°C.

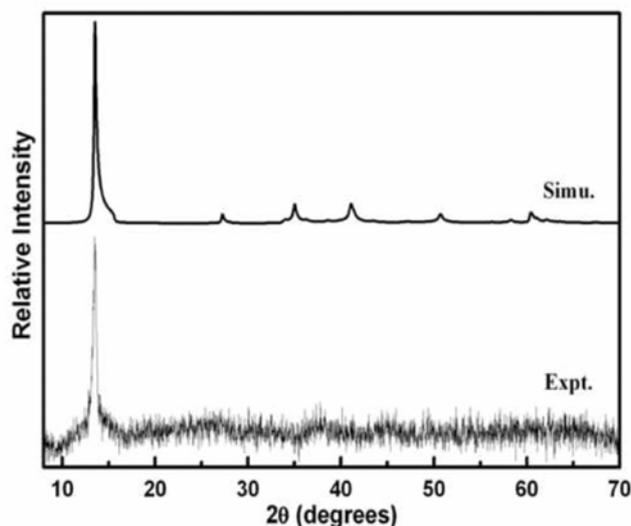
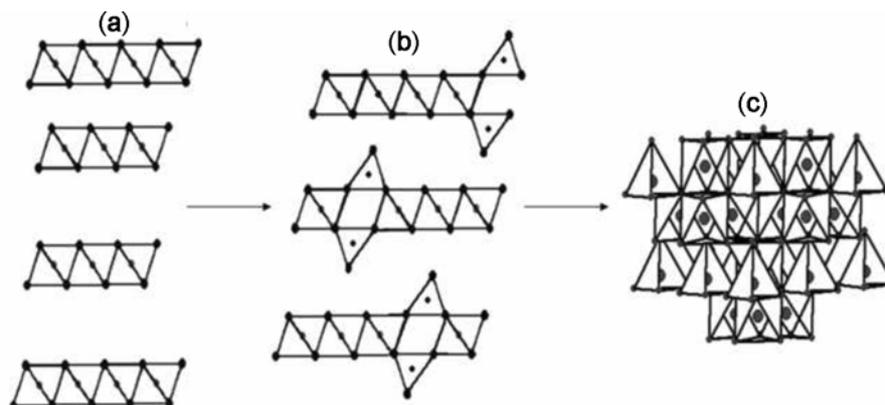


Figure 5. DIFFaX simulated PXRD pattern for the Co–Al– CO_3^{2-} LDH at 200°C compared with its observed pattern.

Table 1. Results of DIFFaX simulations of the PXRD patterns of the calcined $\text{Co}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot m\text{H}_2\text{O}$ LDH.

T (°C)	Disorder	Interlayer water (m)	Crystallite size (Å)		Line shape
			Disc dia (Å)	Layer thickness (Å)	
50	$3R_1$ with 12% $2H_1$	0.64	∞	∞	pseudo-Voigt
150	$3R_1$ with 30% turbostratic disorder	0.52	∞	∞	pseudo-Voigt
175	$3R_1$ with 50% turbostratic disorder	0.22	∞	∞	pseudo-Voigt
200	Aperiodic layers	0	8000	∞	Lorentzian

**Figure 6.** Schematic representation of the structural transformation taking place during the calcination of the Co-Al-CO_3^- LDH: (a) $3R_1$ polytype, (b) hydroxide phase and (c) spinel (Interlayer atoms in (a) and (b) are removed for the purpose of clarity).

temperatures. Hence increase in entropy on heating the Co–Al LDH up to 125°C manifests itself by the increasing incidence of the $2H_1$ stacking faults in $3R_1$ polytype. At 150°C, the LDH begins to lose water from the interlayer, which decreases the occupancy of the interlayer oxygen sites. This is expected to affect the hydroxide layer stacking as the interlayer oxygen atoms are involved in H -bond formation, which is a directive force for the layer stacking in LDHs. The friction and drag involved during this topotactic dehydration of Co–Al LDH leads to the turbostratic disorder in the samples heated to 150–175°C.

Heating of the Co–Al LDH to 200°C leads to the formation of a dehydrated hydroxide phase. The complete removal of the intercalated water reduces the basal spacing from 7.6 Å to 6.6 Å. DIFFaX simulation of this dehydrated phase suggests a structure formed by the regular stacking of aperiodic hydroxide layers. We have generated aperiodic layers by locating randomly chosen Co^{2+} ions in tetrahedral sites in the interlayer. There could be other ways of generating aperiodicity in the metal hydroxide layer. We have chosen this model for the following reasons:

(I) The end product of the decomposition reaction is an oxide with the spinel structure. In the spinel, Co^{2+} ions are distributed in tetrahedral sites and Co^{3+} in octahedral sites. Earlier work (Thomas *et al* 2006) has shown that

the structure of the oxide dictates the structural transformations taking place in the parent hydroxide prior to the decomposition reaction. Thus a metal hydroxide layer with Co^{2+} ions distributed in octahedral and tetrahedral sites has a topochemical relationship with the spinel.

(II) The migration of Co^{2+} ions is also plausible given that Co^{2+} adopts both octahedral and tetrahedral coordination.

In this model, the $\text{Co}^{\text{tetra}}\text{-O}$ bond distances at 1.554 Å are much shorter than those expected of similar bonds in α -cobalt hydroxide (Ma *et al* 2006). This unacceptably short contact, calculated for an ordered stacking, is actually responsible for the introduction of turbostratic disorder in the dehydrated phase. Turbostratic disorder, we believe, plays a crucial role in relaxing the contact distances to acceptable values, although, we have no method of calculating them for a disordered phase. A schematic representation of this transformation starting from the Co–Al LDH is given in figure 6. This figure demonstrates the structural correlation between the hydroxide phase prior to the oxide formation and the spinel phase.

4. Conclusions

The thermal decomposition of Co-Al-CO_3^- LDH to the spinel takes place through a hydroxide phase comprised of a stacking of aperiodic layers. This hydroxide phase

formed prior to the oxide formation comprises of hydroxide layers with Co^{2+} ions distributed in octahedral and tetrahedral sites. The cation distribution in this phase resembles that in the spinel phase and hence this phase acts as an essential precursor for topotactic formation of normal mixed spinel phase.

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