

THERMOGRAVIMETRIC ANALYSIS OF HYDROTALCITES BASED ON THE TAKOVITE FORMULA $\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$

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High resolution thermogravimetric analysis (HRTG) coupled to a gas evolution mass spectrometer has been used to study the thermal decomposition of zinc-modified takovites of formulae $(\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O})$ where x varies from 0 to 6. X-ray diffraction data indicate an increase in the crystallinity and decrease in the interlayer spacing of the materials with increase in the zinc composition. HRTG and mass spectrometry results indicate that water is lost in two major steps, with carbon dioxide coming off simultaneously at the second step. Further loss of CO_2 occurred at higher temperatures due to decomposition of carbonate chemically bound to layer Zn^{2+} and Al^{3+} cations. The variations of the temperatures of dehydration and dehydroxylation/decarbonation with the zinc composition are discussed in terms of the effects of stabilisation of the layer structure, the electronegativity of the layer metals, the charge-to-size ratio of the layer cations and the layer-interlayer hydrogen bonding interactions.

Keywords: decomposition reactions, high-resolution thermogravimetric analysis, mass spectrometric analysis, takovite, zinc-substituted hydrotalcites

Introduction

Interest in the study of hydrotalcites results from their potential use as catalysts [1–5]. The reason for the potential application of hydrotalcites as catalysts rests with the ability to make mixed metal oxides at the atomic level, rather than at a particle level. There are many other uses of hydrotalcites. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite [6, 7]. Hydrotalcites may also be used as components in new nano-materials such as nano-composites [8]. Hydrotalcites are important in the removal of environmental hazards in acid mine drainage [9, 10]. Hydrotalcite formation also offers a mechanism for the disposal of radioactive wastes [11]. Hydrotalcite formation may also serve as a means of heavy metal removal from heavy metal contaminated waters [12]. These hydrotalcites are readily synthesised by a co-precipitation method [13–15].

Hydrotalcites, or layered double hydroxides (LDH) are fundamentally anionic clays, and are less well-known and more diffuse in nature than cationic clays like smectites [16, 17]. The structure of hydrotalcite can be derived from a brucite structure $(\text{Mg}(\text{OH})_2)$ in which, for examples, Al^{3+} or Fe^{3+} (pyroaurite- sjögrenite) substitutes a part of the Mg^{2+} . This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [18, 19]. In hydrotalcites,

a broad range of compositions are possible of the type $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion [20].

The use of thermal analysis techniques for the study of the thermal decomposition of hydrotalcites is not uncommon [21]. Heating sjögrenite or pyroaurite at $<200^\circ\text{C}$ caused the reversible loss of H_2O . At $200\text{--}250^\circ\text{C}$ on static heating, or $200\text{--}350^\circ\text{C}$ on dynamic heating, very little H_2O or CO_2 were lost, but changes in the infrared spectrum and DTA effects were observed. To date, the number of thermal analysis studies of these minerals is very limited. Thermal analysis has been applied to the study of complex mineral systems [22–28]. No studies of the thermal decomposition of zinc-modified takovites have been forthcoming. In this study, the thermal decomposition of synthesised takovite and zinc-substituted takovites was investigated using high resolution thermogravimetric analysis and mass spectrometry of the evolved gases. Such investigation will be quite useful for the development of the materials for potential applications as catalysts and catalyst precursors and as components in new nano-composites.

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Experimental

Synthesis of hydrotalcites

The hydrotalcites were synthesised by the co-precipitation method. Hydrotalcites with a composition of $\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ where x varied from 6 to 0, were synthesised. Two solutions were prepared, namely solution 1 containing 2M NaOH and 0.125M Na_2CO_3 and solution 2 containing 0.75M Ni^{2+} ($\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) and 0.75M Zn^{2+} ($\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) together with 0.25M Al^{3+} (as $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$). Solution 2 in the appropriate ratio was added to solution 1 using a peristaltic pump at a rate of $40\text{ cm}^3\text{ min}^{-1}$, under vigorous stirring, maintaining a pH of 10. To prepare hydrotalcites with different molecular formulae, the ratio of $[\text{Ni}^{2+}]/[\text{Zn}^{2+}]$ was varied according to the required formula. In this way, seven hydrotalcites with Ni:Zn ratios of 6:0, 5:1, 4:2, 3:3, 2:4, 1:5 and 0:6 were prepared. The precipitated minerals are washed at ambient temperatures thoroughly with water to remove any residual nitrate. The composition of the hydrotalcites was checked by ICP and ICP-AES analysis. The phase composition was checked by X-ray diffraction.

Thermogravimetry

Differential thermal and thermogravimetric analyses of the hydrotalcites were obtained using a TA[®] instruments Inc. Q500 high resolution TGA operating at high resolution ramp $10^\circ\text{C min}^{-1}$ resolution 6.0°C from room temperature to 1000°C in a high purity flowing nitrogen atmosphere ($80\text{ cm}^3\text{ min}^{-1}$). Approximately 50 mg of sample was heated in an open platinum crucible. No preparation was required other than grinding the sample up finely. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases evolved, namely water vapour, carbon dioxide and oxygen, were measured.

Results and discussion

X-ray diffraction

It is important to ensure that the synthesized hydrotalcites are layered structures. This was achieved using X-ray diffraction (XRD). The XRD patterns obtained are shown in Fig. 1. As illustrated in Fig. 1, the XRD $d(003)$ peak becomes sharper with increase in the moles of Zn, indicating an increase in the crystallinity. Conversely, a decrease in the moles of Zn leads to the broadening of the peak, indicating a more disordered structure or a decrease in crystallinity. The stabilization of the layered structure with increase in the moles of Zn may be attributed to the lower electronegativity of Zn (1.65) than that of Ni (1.91). The lower electronegativity value

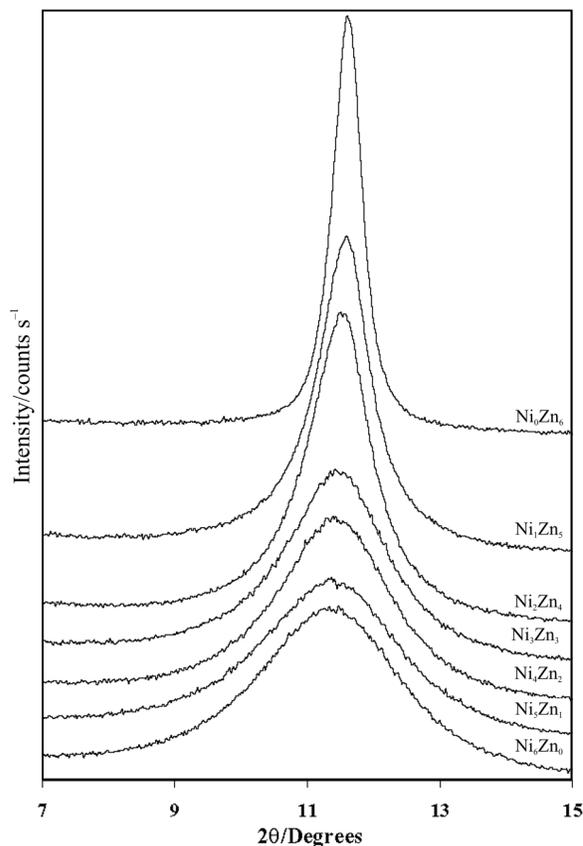


Fig. 1 Powder X-ray diffraction [001] peak of Ni-Zn/Al hydrotalcites

for Zn makes the OH groups to be more strongly bound to Zn, resulting in the stabilization of the layered structure. There is also an apparent linear relationship between the moles of zinc and the $d(003)$ spacing. Increasing the moles of Zn substituted for Ni in the takovite formula results in the decrease of the $d(003)$ spacing. The linear relationship is found to be $y = -0.0374x + 7.827$ with R^2 value of 0.9847, where y is the $d(003)$ spacing and x is the moles of zinc. The significance of this result is that not only are the interlayer spacings of hydrotalcites anion dependent but they are also cation dependent, as reported recently [30]. The lowering of the basal spacing with increase in the moles of zinc may be related to the bigger ionic size of Zn^{2+} (0.74 Å) compared with that of Ni^{2+} (0.69 Å). The bigger ionic size of Zn^{2+} makes the layer thickness to increase leading to the ultimate reduction in the interlayer spacing. The interlayer spacing is thus progressively reduced as the moles of Zn is increased.

High-resolution thermogravimetric analysis

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of zinc modified takovites of formula $\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ are shown

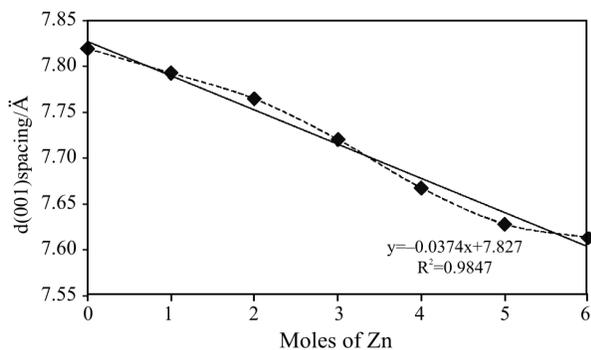


Fig. 2 Plot of d(001) spacing against the moles of zinc for the Ni-Zn/Al hydrotalcites. The broken line is the curve passing through the experimental points while the solid line is the linear trendline through the points

in Figs 3a to 3g. The results of the thermogravimetric analyses are reported in Table 1. For takovite, $(\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O})$, two mass loss steps are observed at 91.06 and 284.65°C with mass losses of 14.35 and 17.70%. The theoretical mass loss for the first step is 8.89%. This mass loss is attributed to dehydration. However, the higher experimental value than the theoretical figure for this mass loss suggests that some dehydroxylation may also be possible at this step. The second mass loss step occurs at 284.65°C with a mass loss of 17.70%. This may be compared with a theoretical mass loss of 23.21%. The theoretical mass loss for steps 1 and 2 is 32.1%. The

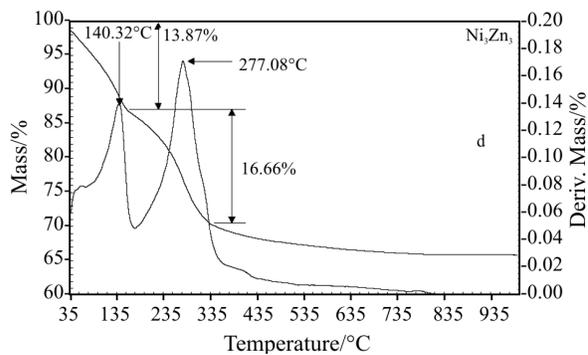
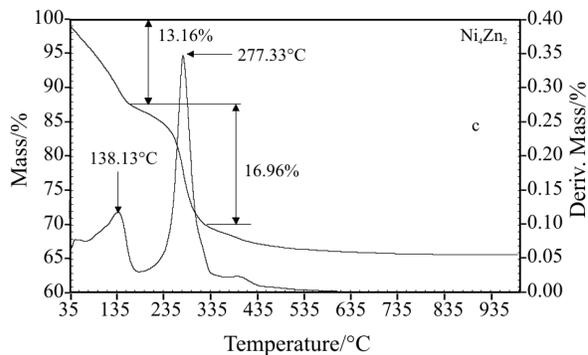


Fig. 3c, 3d TG and DTG curves for c – 4:2 Ni-Zn/Al hydrotalcite; d – 3:3 Ni-Zn/Al hydrotalcite

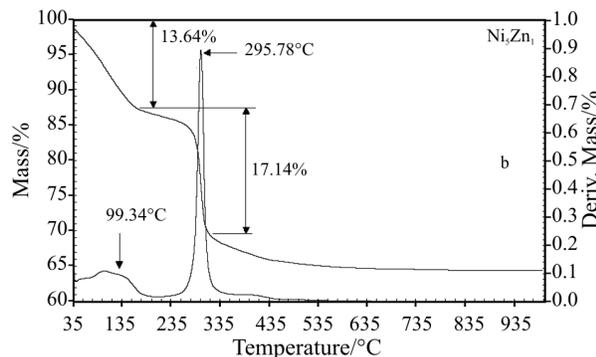
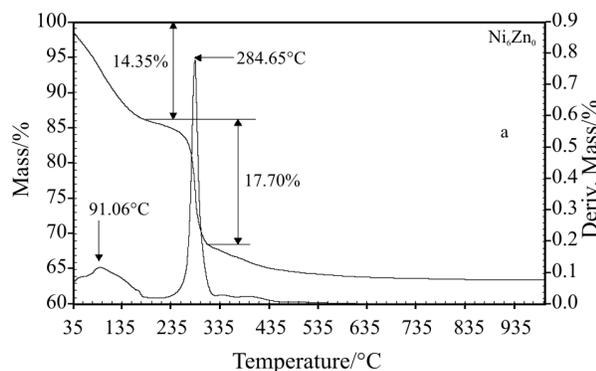


Fig. 3a, 3b TG and DTG curves for a – Ni/Al hydrotalcite (takovite); b – 5:1 Ni-Zn/Al hydrotalcite

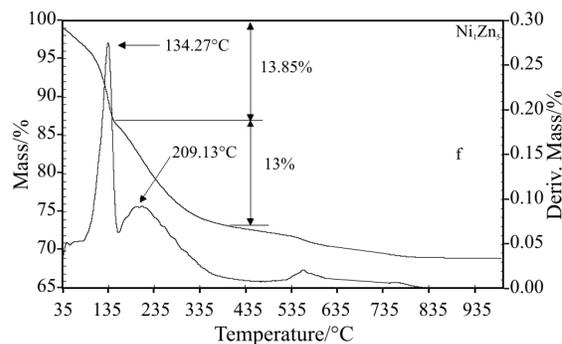
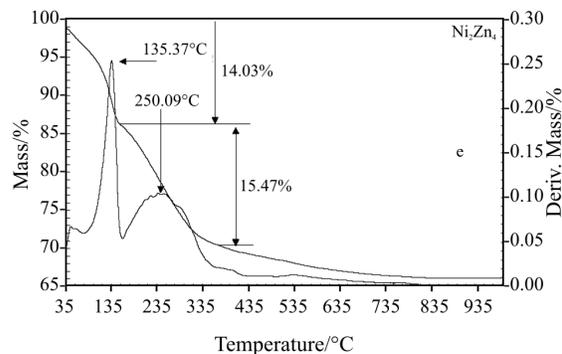


Fig. 3e, 3f TG and DTG curves for e – 2:4 Ni-Zn/Al hydrotalcite; f – 1:5 Ni-Zn/Al hydrotalcite

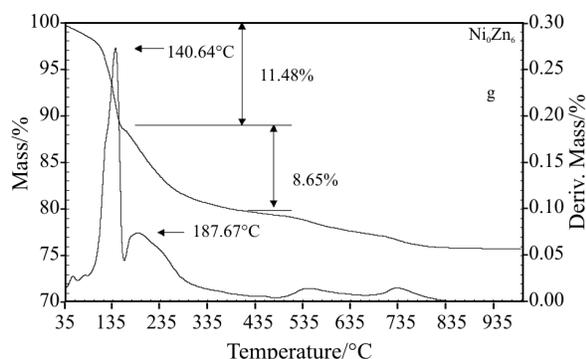


Fig. 3g TG and DTG curves for Zn/Al hydrotalcite

experimental mass loss for steps 1 and 2 is 32.05%, in agreement with the theoretical value of 32.1%. The second mass loss step is attributed to the loss of the hydroxyl units and interlayer carbonate. These two units appear to be lost simultaneously.

For the other hydrotalcites of formula $\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$, two mass loss steps are also identified. The first, as in the case of takovite, is attributed to dehydration although the results above suggest that some dehydroxylation may also take place at the lower temperatures. The second step for the Zn-substituted takovites is also attributed to the combination of dehydroxylation and decarbonation. The data in Table 1 suggests that there is a relationship between the temperature of dehydration and the moles of Zn. Such a relationship is shown in Fig. 4a. The temperature of dehydration increases with the moles of Zn substituted. The data may be fitted to a linear function $y=8.7251x+92.216$ with an R^2 value of 0.9578, where y is the temperature of dehydration and x is the moles of Zn. This observation may be related to the lowering of the interlayer spacing with increase in moles of zinc. The reduction in the interlayer spacing on Zn incorporation would favour stronger hydrogen bond interactions between the interlayer water molecules and stronger hydrogen bonding of the water molecules with the interlayer carbonate ions or

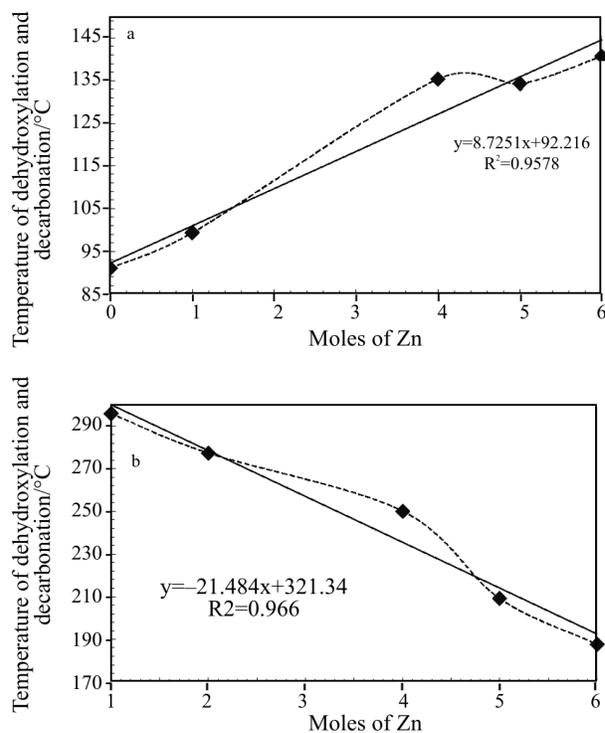


Fig. 4 Plots of the temperature of a – dehydria/dehydroxylation and b – dehydroxylation/decarbonation against the moles of zinc for the Ni–Zn/Al hydrotalcites. The broken lines are the curves passing through the experimental points while the solid lines are the linear trendlines through the points

even with layer hydroxyl groups. In contrast, however, the temperature of dehydroxylation/ decarbonation was found to decrease linearly with increase in the moles of zinc substituted into the takovite formula as shown in Fig. 4b. The data is fitted to a linear function $y=-21.484x+321.34$ with an R^2 value of 0.966, where again y is the temperature of dehydroxylation/ decarbonation and x is the moles of zinc. On going from the zinc-substituted hydrotalcite formula ($\text{Ni}_5\text{Zn}_1\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$) with one mole of zinc to ($\text{Zn}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$), the temperature of the

Table 1 Results of weight losses of the TG and DTG for Ni/Zn/Al hydrotalcites

	Step 1: Dehydration & Dehydroxylation			Step 2: Dehydroxylation & Decarbonation		
	Weight loss %		Temp./°C	Weight loss %		Temp./°C
	found	theor.		found	theor.	
Ni_6Zn_0	14.35	8.89	91.06	17.70	23.21	284.65
Ni_5Zn_1	13.64	8.81	99.34	17.14	23.02	295.78
Ni_4Zn_2	13.16	8.74	138.13	16.96	22.82	277.33
Ni_3Zn_3	13.87	8.67	140.32	16.66	22.64	277.08
Ni_2Zn_4	14.03	8.60	135.37	15.47	22.46	250.09
Ni_1Zn_5	13.85	8.53	134.27	13	22.29	209.13
Ni_0Zn_6	11.48	8.47	140.64	8.65	22.12	187.67

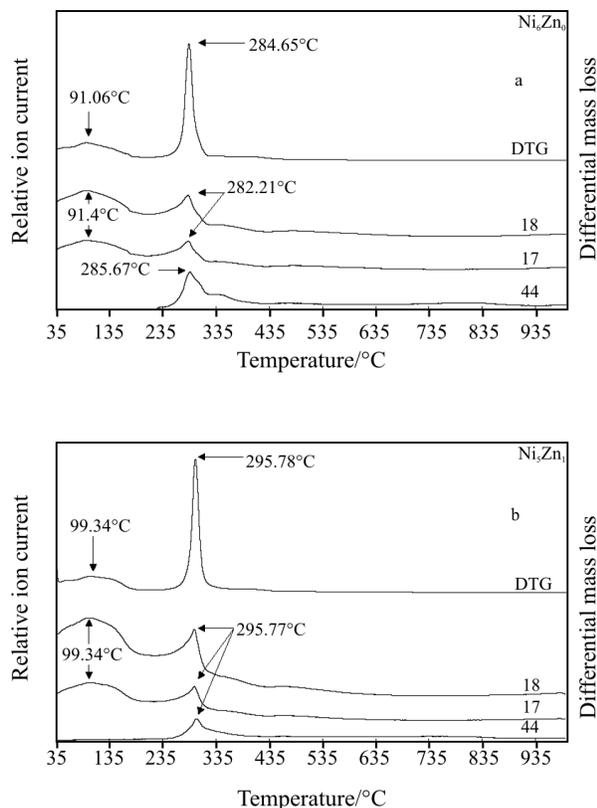


Fig. 5a, 5b DTG and MS curves for a – Ni/Al hydrotalcite (takovite); b – 5:1 Ni–Zn/Al hydrotalcite

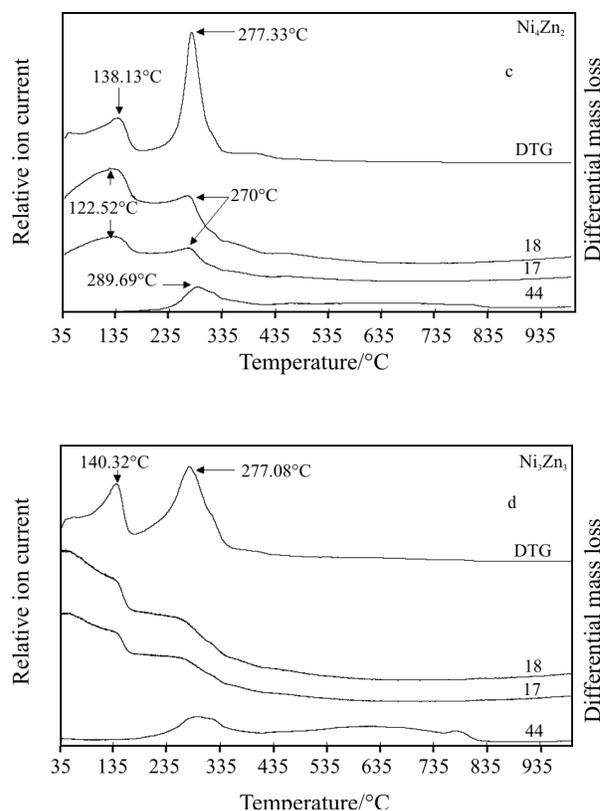


Fig. 5c, 5d DTG and MS curves for c – 4:2 Ni–Zn/Al hydrotalcite; d – 3:3 Ni–Zn/Al hydrotalcite

dehydroxylation/decarbonation is observed to decrease significantly from 295.78 to 187.67°C. However, the dehydroxylation/decarbonation temperature increases from 284.65 to 295.78°C on going from $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ to $\text{Ni}_5\text{Zn}_1\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$ by incorporation of only one mole of zinc into the takovite formula. The incorporation of Zn^{2+} with lower charge-to-size ratio than Ni^{2+} would facilitate the process of decarbonation due to the weakening of the interaction between the layers and the interlayer carbonate. This effect therefore appears to compete strongly with the effects of stabilization of the layered structure and stronger hydrogen bonding interactions that lead to increase in the temperature of dehydration in zinc-substituted takovites. These results thus provide a measure of the stability of takovite compared with zinc-substituted takovites. It appears that the effect of stronger interaction of the interlayer carbonate with the layer cations predominates in the takovite during the process of dehydroxylation/decarbonation. Thus, the takovite is more stable than the zinc-substituted hydrotalcites with respect to dehydroxylation/decarbonation. However, the 5:1 Ni–Zn hydrotalcite has a higher temperature of dehydroxylation/decarbonation and therefore slightly more stable than takovite containing no zinc due to the pre-

vailing effects of the stabilization of layer structure and hydrogen bonding interactions resulting from zinc incorporation. On the other hand, the effects of stabilization of the layered structure and stronger hydrogen bonding interactions by zinc incorporation predominate in the process of dehydration such that the zinc-substituted hydrotalcites are more stable than the takovite.

In addition to the two steps of dehydration and dehydroxylation/decarbonation, three higher temperature mass losses are also observed at about 300°C, 550–560°C and 735–765°C in the Zn-substituted takovites containing higher moles of Zn, i.e. Ni_2Zn_4 , Ni_1Zn_5 and Ni_0Zn_6 (Figs 3e to 3g). These secondary higher temperature losses are ascribed to further loss of interlayer carbonate. This is confirmed later in section 3.3 by mass spectrometric (MS) analysis of evolved gases that shows that CO_2 gas is evolved at these temperatures. It is suggested that during the dehydroxylation and decarbonation of these Zn-substituted takovites, some of the carbonate ions are forced to bond chemically to the layer cations to form molecules such as NiCO_3 , ZnCO_3 , and $\text{Al}_2(\text{CO}_3)_3$. The 300°C peak overlaps with the dehydroxylation step in Ni_2Zn_4 takovite (Fig. 3e), and is virtually absent in Ni_1Zn_5 and Ni_0Zn_6 . On the basis of this observation

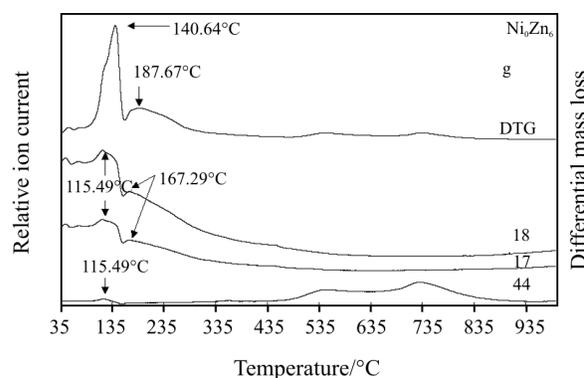
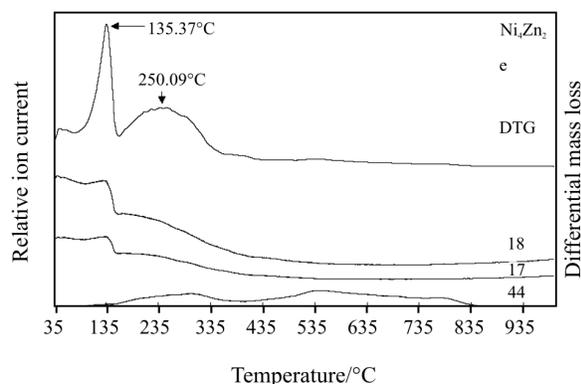


Fig. 5g DTG and MS curves for g – Zn/Al hydroxalcite

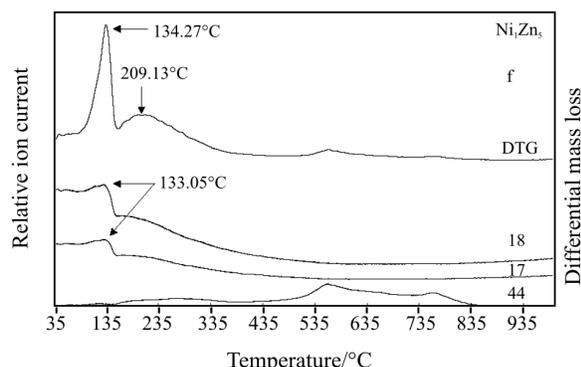


Fig. 5e, 5f DTG and MS curves for e – 2:4 Ni–Zn/Al hydroxalcite; f – 1:5 Ni–Zn/Al hydroxalcite

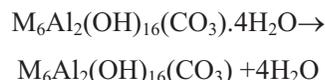
and the fact that the electronegativity of the metals reduces in the order Ni>Zn>Al, the higher temperature mass losses at 300°C, 550–560°C and 735–765°C are assigned to loss of carbonate bound to Ni²⁺, Zn²⁺ and Al³⁺ cations, respectively. The gradual decrease in the mass loss in step 2 due to dehydroxylation/ decarbonation on increasing the moles of Zn from 0 to 6 (Table 1 and Figs 3, 4), may therefore be attributed to this higher temperature loss of carbonate ions bound to the layer cations. The experimental total mass loss for steps 1 and 2 for Ni₁Zn₅ (26.85%) and Ni₀Zn₆ (20.13%) are lower than the theoretical values of 30.82% and 30.59%, respectively due to this higher temperature secondary loss of carbonate ions bound to layer cations. In the case of the other Zn-substituted takovites, the experimental total mass losses for steps 1 and 2 compare well with the theoretical values.

Mass spectrometric analysis

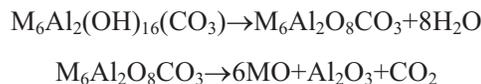
The DTG of the takovites and MS curves of CO₂ (MS=44), H₂O (MS=18) and OH (MS=17) are shown in Figs 5a to 5g. It is a fundamental principle that the mass spectrometric curves follow the DTG curves. Figs 5a to 5g show that the patterns of the DTG and MS curves are identical. The MS results also show

that water is lost in two major steps at 90–150°C and 160–300°C while carbon dioxide comes off at about 200–300°C, in agreement with the TG/DTG data. The MS data therefore confirms that the first step is the dehydration step and second step the dehydroxylation/decarbonation step. Again, as observed in the TG/DTG results, the MS curves for the Zn-substituted takovites containing 4 to 6 moles of Zn show further higher temperatures loss of CO₂ at about 550–560°C and 735–765°C thereby confirming the loss of carbonate chemically bound to layer Zn²⁺ and Al³⁺ cations, respectively. The following chemical reactions are therefore proposed for the thermal decomposition of the synthesized takovite or Zn–Al hydroxalcite:

Decomposition Step 1 at 91.06 (Ni₆Zn₀) or 140.64°C (Ni₀Zn₆)



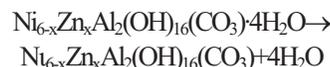
Decomposition Step 2 at 284.65 (Ni₆Zn₀) or 184.67 (Ni₀Zn₆)°C



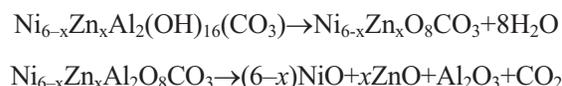
where M=Ni or Zn.

For the Ni–Zn–Al hydroxalcites, the proposed chemical reactions can be represented as:

Decomposition Step 1 at 99–134°C



Decomposition Step 2 at 209–295°C



Conclusions

A series of nickel-based aluminium hydrotalcites of formulae $\text{Ni}_x\text{Zn}_{6-x}\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ with zinc substitution have been studied by high resolution thermogravimetry and mass spectrometric analysis of evolved gases. Powder X-ray diffraction was also used to determine the crystallinity and interlayer spacing of the materials. The results of the investigation can be summarized as follows:

The X-ray diffraction data show that the crystallinity of the materials increases and the interlayer spacing decreases linearly with increase in the moles of zinc incorporated into the formula. The lower electronegativity value for Zn than that of Ni makes the OH groups to be more strongly bound to Zn, resulting in the stabilization of the layered structure. Also, the bigger ionic size of Zn^{2+} compared with Ni^{2+} causes the layer thickness to increase such that there is ultimate reduction in the interlayer spacing.

TG/DTG and mass spectrometric analysis of evolved gases indicate that that water is lost in two major steps at 90–150 and 160–300°C, while carbon dioxide is lost simultaneously at the second step at 200–300°C. The first step is due to dehydration while the second step is attributed to dehydroxylation/ decarbonation.

Further secondary loss of CO_2 was also observed at higher temperatures of about 550–560 and 735–765°C due to decomposition of carbonate ions chemically bound to layer Zn^{2+} and Al^{3+} cations, respectively.

While the temperature of dehydration was observed to increase linearly with increase in the composition of zinc in the takovite formula, the temperature of dehydroxylation/decarbonation was found to decrease linearly with increase in moles of zinc from 5:1 Ni–Zn/Al hydrotalcite. These observations are related to the differences in the charge-to-size ratios of the cations and the prevailing effects of stabilization of the layered structure and hydrogen bonding interactions on zinc incorporation.

Acknowledgments

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