Thermal behaviour of hydroxides, hydroxysalts and hydrotalcites

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Abstract. Mass spectrometric analysis of gases evolved during thermal decomposition of divalent metal hydroxides, hydroxysalts and hydrotalcites show that all these compounds undergo dehydration in the temperature range $30 < T < 220°C$ followed by decomposition at temperatures above $250°C$. The latter step involves simultaneous deanation and dehydroxylation of the layers. Our observations conclusively prove that alternative mechanisms which envisage CO_2 evolution due to deanation at lower temperatures proposed by Kanezaki to be wrong.

Keywords. Hydroxides; hydrotalcites; temperature programmed decomposition (TPD).

1. Introduction

Hydroxides $[M(OH)_2]$, hydroxysalts $[M(OH)_{2-x}(A^{n-})_{x/n} \cdot mH_2O$, where $x = 0.5–1.0]$ and hydrotalcite-like layered double hydroxides $[M^{II}_{1-x}M'^{III}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$, where $M^{II} = $ Mg, Co, Ni, Cu, Zn or Cd, $M^{III} = $ Al, V, Cr, Fe or Ga and $x = 0.25–0.33]$ derive their structures from that of mineral brucite, $[Mg(OH)_2]$. In brucite, OH^- ions are hexagonally close packed and Mg^{2+} ions occupy alternate layers of octahedral sites resulting in a stacking of charge-neutral layers of the composition $[Mg(OH)_2]$ ($P\bar{3}m1$, $a = 3.01$ Å and $c = 4.8$ Å) (Oswald and Asper 1977).

While the **b**-hydroxides of nickel and cobalt are isostructural with brucite, in the **a**-hydroxides, a fraction, x, of the hydroxyl ions are protonated leading to positively charged layers of the composition $[M(OH)_{2-x}(H_2O)_x]^{x+}$. Anions and water molecules are incorporated in the interlayer region for charge balance and stability leading to an increased interlayer spacing ($c/3 = 7.6$ Å when the anion is CO_3^{2-}) (Kamath et al 1997).

When a fraction, x, of the hydroxyl ions of the brucite layer is replaced by anions, the layer composition becomes $[M(OH)_{2-x}(A^{n-})_{x/n}]$. Here the anions are grafted to the metal ions and such materials are referred to as hydroxysalts (Gallezot and Prettre 1969). Water molecules may be incorporated in the interlayer region for stability.

In hydrotalcite-like layered double hydroxides, a fraction, x, of the M^{2+} ions of the brucite layers are isomorphously substituted by M'^{3+} ions to give the layer composition $[M^{II}_{1-x}M'^{III}_x(OH)_2]^{x+}$. Anions and water molecules are incorporated in the interlayer region (Cavani et al 1991).
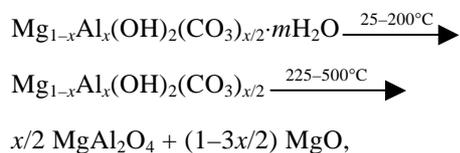
These hydroxide materials are used as precursors for oxide catalysts (Baird et al 1997) and the catalytic activity of the oxide catalysts depends on the structure, composition, morphology and thermal history of the precursor. It is, therefore, important to understand the structural and compositional changes that occur during the hydroxide decomposition. Considerable work has been done to understand the thermal behaviour of hydroxide based materials (Cavani et al 1991).

Most hydroxide materials considered here yield oxides on thermal decomposition above $500°C$. While the hydroxides and hydroxysalts yield the corresponding metal oxides, the hydrotalcites yield a mixture of the divalent metal oxide ($M^{II}O$) and the mixed metal spinel ($M^{II}M'^{III}O_4$). The hydroxide to oxide conversion has been extensively studied by thermogravimetry and involves a number of competing reactions such as dehydration, deanation of the interlayer region and dehydroxylation of the brucite slabs. These processes may occur in separate or combined steps. It is generally believed that dehydration precedes the deanation–dehydroxylation step. However, there is no direct evolved gas analysis data as evidence to support this belief. In many systems one or more of these steps can be reversed either by simply cooling (Puttaswamy and Kamath 1997) or by treating the oxide residue in water (Sato et al 1986). Reversible thermal behaviour has been established both by weight gain data as well as by variable temperature X-ray powder diffraction (Constantino and Pinnavaia 1995).

Considerable confusion regarding our understanding of the thermal behaviour of hydroxide materials was created by a recent series of papers by Kanezaki (1998a–d), who

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proposed that deanation precedes dehydration by a novel chemical reaction between the intercalated anions and water molecules, thus eliminating the dehydration step entirely. While the generally accepted mechanism for the decomposition of carbonate containing Mg–Al hydrotalcite is

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O \xrightarrow{25-200°C}$$

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \xrightarrow{225-500°C}$$

$$x/2 \; MgAl_2O_4 + (1-3x/2) \; MgO,$$

Kanezaki proposed that the decomposition takes place as

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O \xrightarrow{25-200°C}$$

$$Mg_{1-x}Al_x(OH)_{2+x} \cdot yH_2O \xrightarrow{225-500°C} x/2 \; MgAl_2O_4$$
(Kanezaki phase II)

$$+ (1-3x/2) \; MgO,$$

where $y = m - x/2$ and suggested that CO_2 is evolved in the first step due to the reaction

$$CO_3^{2-} + H_2O \rightarrow CO_2\uparrow + 2OH^-.$$

In order to understand which of these mechanisms is correct, we have carried out temperature programmed decomposition (TPD) of the title hydroxide materials coupled with mass spectrometric analysis of the evolved gases.

2. Experimental

b-Hydroxides of nickel and cobalt were obtained from Aldrich, USA. *a*-Nickel hydroxide was prepared by cathodic deposition from a nickel nitrate solution (Jayashree and Kamath 1999a). *a*-Cobalt hydroxide was prepared by
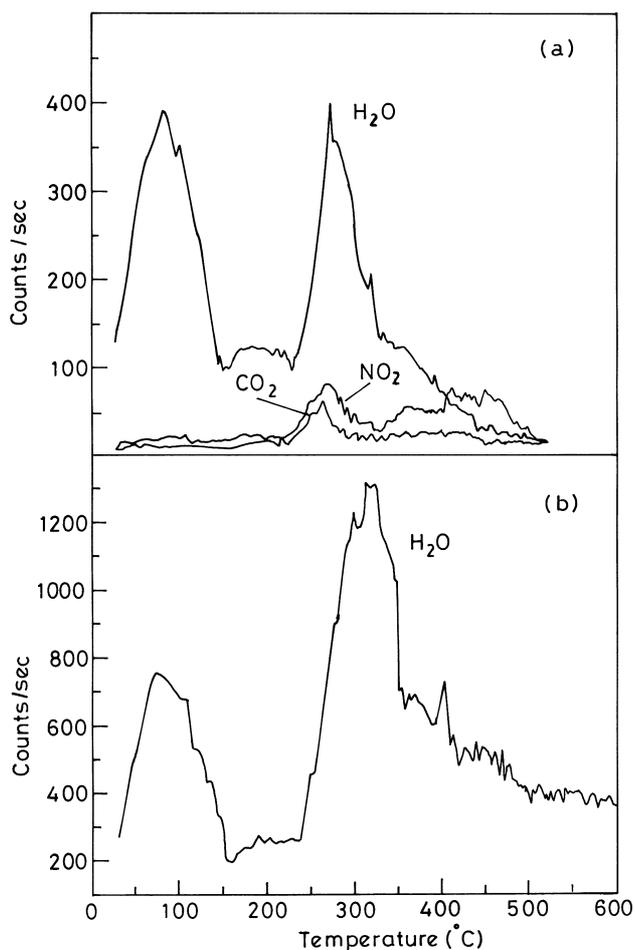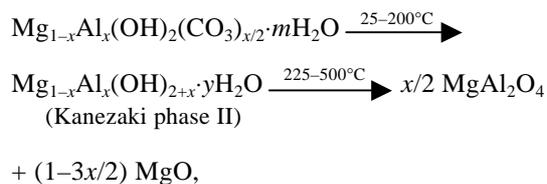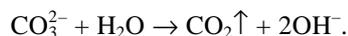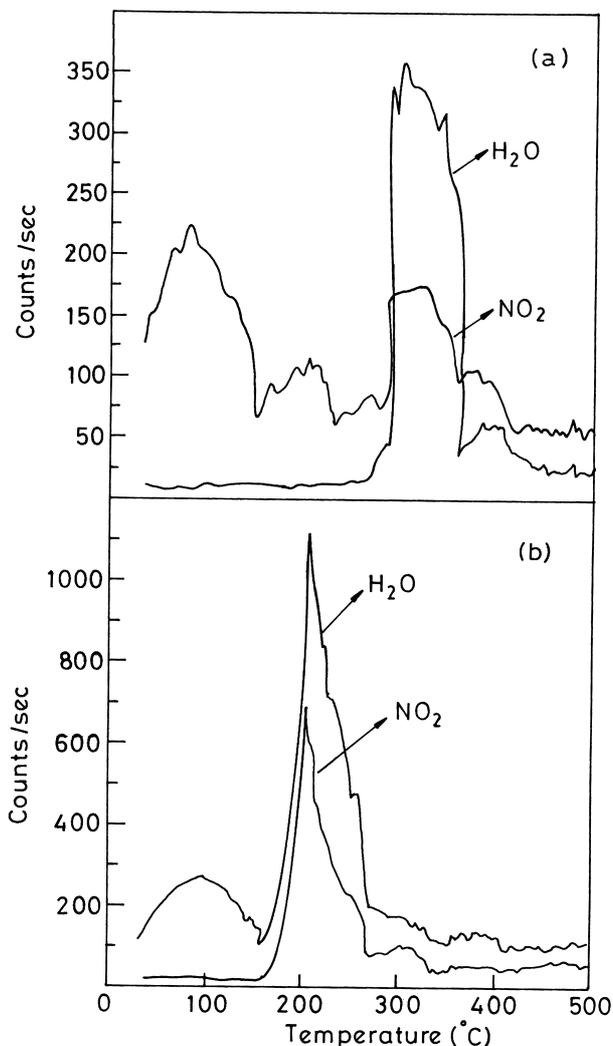

Figure 1. Temperature profiles of the gases evolved during the thermal decomposition of *a*-nickel hydroxide (**a**) and *b*-nickel hydroxide (**b**).

Figure 2. Temperature profiles of the gases evolved during the thermal decomposition of $Ni_3(OH)_4(NO_3)_2$ (**a**) and $Co_3(OH)_4(NO_3)_2$ (**b**).

ammonia precipitation from a cobalt nitrate solution (Rajamathi *et al* 2000). The hydroxysalts, $Ni_3(OH)_4(NO_3)_2$ and $Co_3(OH)_4(NO_3)_2$, were obtained by urea hydrolysis of the corresponding metal nitrate melts (Rajamathi and Kamath 1998). Hydrotalcites, $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$, ($x$ = 0·2, 0·25 and 0·33), $Mg_{1-x}Fe_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$ (x = 0·25), $Ni_{1-x}M_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$ (x = 0·25 and M = Al, Fe), $Co_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$ (x = 0·25) and $Zn_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot mH_2O$ (x = 0·33), were prepared by Reichle's (1986) method.

Materials were characterized by X-ray powder diffraction (JEOL JDP 8X Powder Diffractometer, CuK*a*, *l* = 1·541 Å), infrared spectroscopy (Nicolet Model Impact 400D FTIR, KBr pellets, 4 cm^{-1} resolution) and wet chemical analysis.

In a typical TPD experiment, about 0·2 g of the sample was loaded into a quartz reaction tube in which a fine chromel–alumel thermocouple was immersed into the sample. The reaction tube was evacuated to a base pressure of 10^{-5} torr. The sample was heated from 30 to 750°C at a heating rate of 10°C min^{-1}. The evolved gases were leaked into a ultrahigh vacuum chamber connected to a quadrupole mass spectrometer (Model QXK300, VG Scientific, England). The mass analysis was done every 10s and the data stored in a computer. At the end of the experiment the temperature profile of the evolved gas was obtained from the raw data. The details of this laboratory-built TPD setup are described elsewhere (Hegde *et al* 1992).

3. Results and discussions

3.1 *Thermal behaviour of hydroxides*

In figure 1 are shown the temperature profiles of the gases evolved during the thermal decomposition of *a* and *b*-nickel hydroxides.

Stoichiometric *b*-$Ni(OH)_2$ is expected to undergo a single step decomposition as

$$Ni(OH)_2 \longrightarrow NiO + H_2O.$$

Accordingly the mass spectrum of the gases evolved during the decomposition of *b*-$Ni(OH)_2$ shows only the presence of H_2O (m/e = 18). The temperature profile of water evolved shows a decomposition range of 225–500°C and matches with the TG data (Jayashree and Kamath 1999b). *a*-Nickel hydroxide on the other hand evolves both H_2O and NO_2 (appearing as NO, m/e = 30) on heating. Water is lost in two steps (25–150°C and 225–500°C), while NO_2 (along with trace CO_2) is lost along with the high temperature H_2O species. The low temperature water loss is shown to be reversible by TG
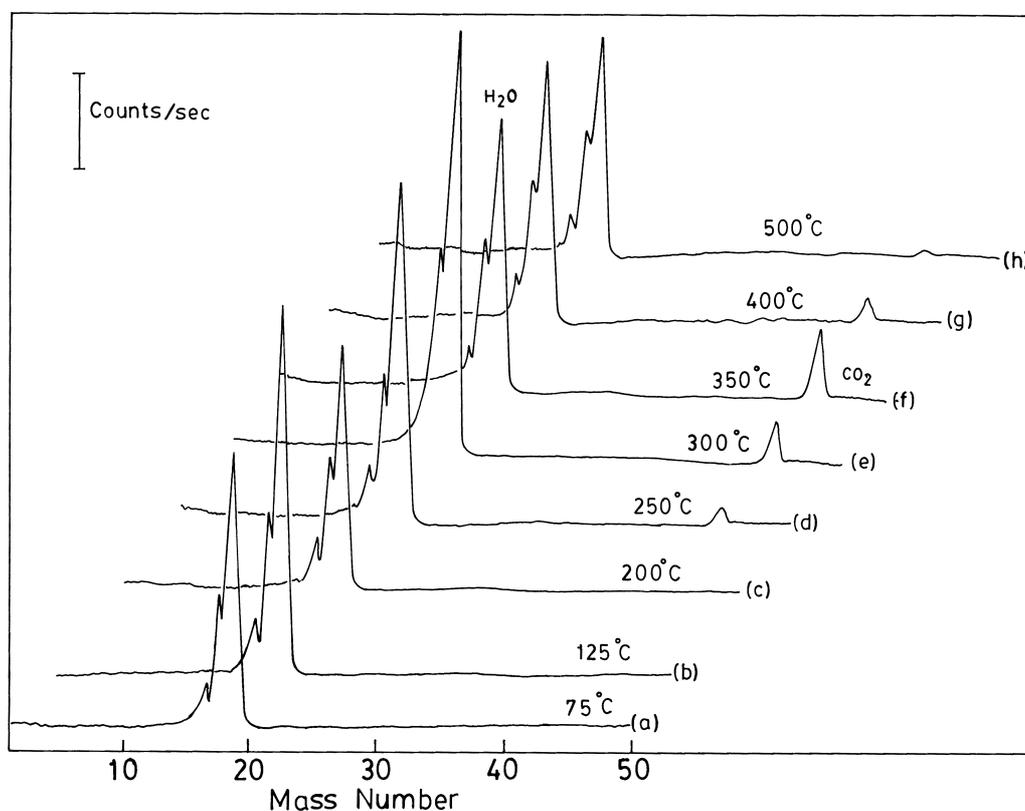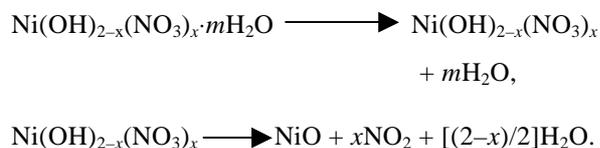

Figure 3. Mass spectra of the gases evolved at various temperatures during the TPD of Mg–Al (x = 0·25) hydrotalcite.

studies (Jayashree *et al* 2000). The sequence of reactions is dehydration followed by simultaneous deanation–dehydroxylation.

$$Ni(OH)_{2-x}(NO_3)_x \cdot mH_2O \longrightarrow Ni(OH)_{2-x}(NO_3)_x$$
$$+ mH_2O,$$

$$Ni(OH)_{2-x}(NO_3)_x \longrightarrow NiO + xNO_2 + [(2-x)/2]H_2O.$$

a and *b*-Hydroxides of cobalt behave similarly except that they decompose at slightly lower temperatures and their decomposition product is the spinel, Co_3O_4.

3.2 *Thermal behaviour of hydroxysalts*

In figure 2 are shown the results of temperature programmed decomposition of the hydroxysalts, $M_3(OH)_4$ $(NO_3)_2$ (M = Co, Ni). TG data (Rajamathi and Kamath 1998, 1999) indicate that these decompose in a single step.

$$Ni_3(OH)_4(NO_3)_2 \longrightarrow 3NiO + 2NO_2 + 4H_2O.$$

Accordingly simultaneous loss of H_2O and NO_2 is observed in the temperature range 275–500°C.

3.3 *Thermal behaviour of hydrotalcites*

Hydrotalcites are known to undergo a two-step weight loss on heating. The low temperature step (25–220°C) has been attributed to loss of intercalated water molecules and the high temperature step (225–450°C) has been attributed to decomposition (Constantino and Pinnavaia 1995). TG studies reported earlier (Puttaswamy and Kamath 1997) show that the hydrotalcites fall into three categories: (i) the hydrotalcites of Mg which show reversible thermal behaviour and reconstruct the parent phase even after the second weight loss, (ii) the hydrotalcites of Ni which show reversibility of the first step only and (iii) the hydrotalcites of Co and Zn which show a single irreversible weight loss.

Figure 3 shows the mass spectra of the evolved gases recorded at different temperatures during the TPD of the Mg–Al hydrotalcite. It is evident that the only gases evolved during decomposition are H_2O ($m/e = 18$) and CO_2 ($m/e = 44$). The temperature profiles of H_2O and CO_2 evolution from the same compound are shown in figure 4. It is evident that up to 250°C, the mass spectra indicate the evolution of only H_2O showing that the Kanezaki phase II which is stable up to 260°C retains all the CO_3^{2-}. CO_2 evolution is observed along with additional water arising out of the dehydroxylation of the hydroxide sheets at temperatures in excess of 250°C. All the hydrotalcites investigated by us showed similar characteristics and no CO_2 evolution was seen in any of the samples at the
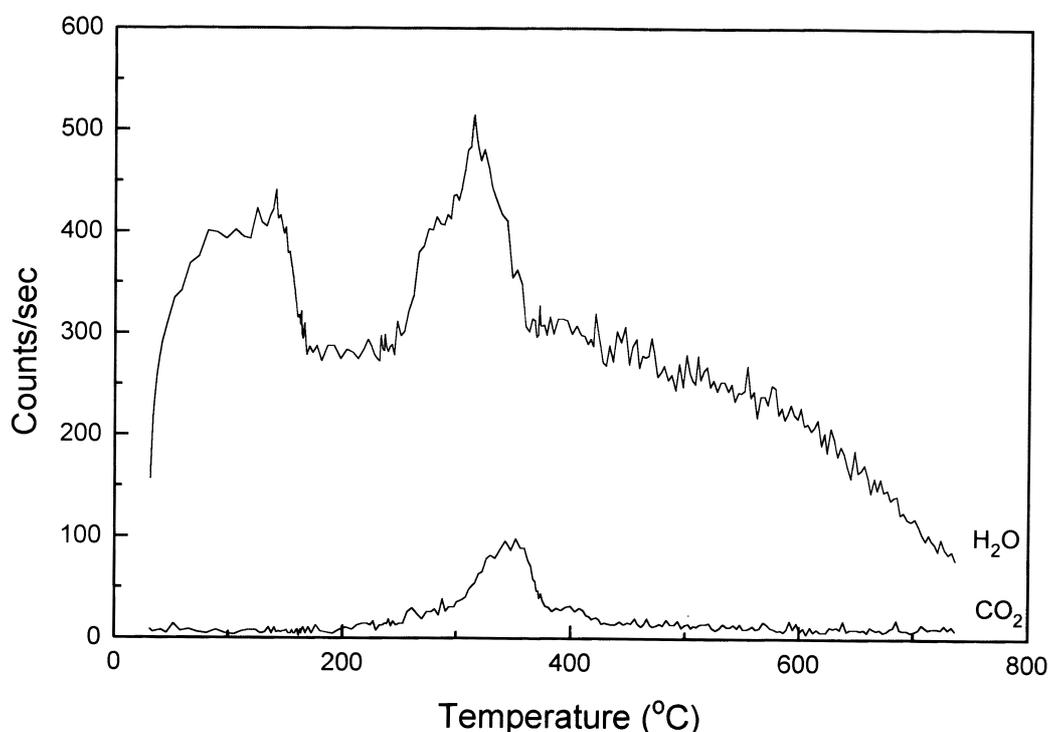

Figure 4. Temperature profiles of the gases evolved during the thermal decomposition of Mg–Al ($x = 0.25$) hydrotalcite.
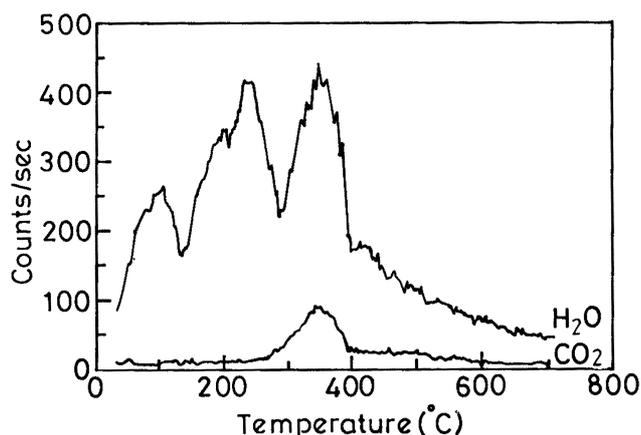
Figure 5. Temperature profiles of the gases evolved during the thermal decomposition of Ni–Al ($x = 0.25$) hydrotalcite.

Table 1. Comparison of TG data with TPD data for hydrotalcites.

Hydrotalcite (composition)	$T°C^a$	$T°C^b$
Mg/Al ($x = 0.33$)	275	275
Mg/Al ($x = 0.25$)	250	260
Mg/Al ($x = 0.20$)	225	275
Mg/Fe($x = 0.25$)	225	300
Ni/Al ($x = 0.25$)	245	275
Ni/Fe ($x = 0.25$)	200	260
Co/Al ($x = 0.25$)	180	250
Zn/Al ($x = 0.33$)	–	200

[a]Temperature at which the first step ends in TG.
[b]Temperature at which CO_2 evolution begins in TPD.

temperature of the first weight loss. Another illustrative example is shown in figure 5 which corresponds to the Ni–Al hydrotalcite. We list in table 1 the temperature at which the first weight loss (as obtained from TG data) (Puttaswamy and Kamath 1997) concludes and compare it with the temperature at which CO_2 evolution begins in all the hydrotalcites studied here. It is evident that the CO_2 evolution occurs only during the second step in all the cases. These results agree with the volumetric estimations of evolved CO_2 performed by Hibino *et al* (1995).

4. Conclusions

We provide direct experimental evidence to show the Kanezaki mechanism of hydrotalcite decomposition inco-

rrect and the widely accepted dehydration–decomposition mechanism correct. The mechanism of decomposition is the same in the related compounds, viz. hydroxides and hydroxysalts.

Acknowledgement

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