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Thermochimica Acta 412 (2004) 149–153
thermochimica acta
www.elsevier.com/locate/tca

Investigation of thermal decomposition of $MgCl_2$ hexammoniate and $MgCl_2$ biglycollate biammoniate by DTA–TG, XRD and chemical analysis

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Received 8 April 2003; received in revised form 23 September 2003; accepted 23 September 2003

Abstract

The decomposition of $MgCl_2{\cdot}6NH_3$ and $MgCl_2{\cdot}2C_2H_6O_2{\cdot}2NH_3$ in static air was investigated by DTA–TG, XRD and chemical analysis from room temperature to 700 °C. The results indicated that $MgCl_2{\cdot}6NH_3$ took three steps to decompose to anhydrous $MgCl_2$ below 450 °C and at higher temperatures resulted in the oxidation of anhydrous $MgCl_2$. This theoretically confirms the validity of the operation in which Ar or N_2 is used in manufacturing anhydrous $MgCl_2$ at 650 °C. $MgCl_2{\cdot}2C_2H_6O_2{\cdot}2NH_3$ experienced a complicated process of decomposition, Mg(OH)Cl and carbon were obtained at 300 °C and MgO at 530 °C, respectively, which may decrease the quality of anhydrous $MgCl_2$.

Keywords: $MgCl_2{\cdot}6NH_3$; $MgCl_2{\cdot}2C_2H_6O_2{\cdot}2NH_3$; Thermal decomposition; Anhydrous $MgCl_2$

1. Introduction

$MgCl_2$ hexammoniate is useful in producing anhydrous $MgCl_2$, which is the commercially efficient origin in preparation of metal magnesium. It was also used to control the temperature of the electrolyte as well as the content of $MgCl_2$ in the process for electrolytically producing magnesium metal [1]. The ammoniate was formed by treating the anhydrous solution of $MgCl_2$ hydrate (e.g. $MgCl_2{\cdot}6H_2O$) in ethylene glycol (with or without ammonium chloride) with an excess amount of ammonia [2,3]. It could also be produced by precipitating $MgCl_2$ in a solution of $MgCl_2$–NH_3–NH_4Cl–CH_3OH–H_2O with ammonium in the solution saturated by ammonium [4]. In the production of magnesium chloride hexammoniate in ethylene glycol, it was pointed out that there were three kinds of complexes, $MgCl_2$ hexammoniate, $MgCl_2$ biglycollate biammoniate and magnesium chloride triglycollate, formed in different reaction conditions, and the XRD pattern of the three compounds were provided [3]. To obtain anhydrous $MgCl_2$, magnesium chloride hexammoniate must be calcined at 450–650 °C [3,4]. However, up to now, there is no detailed information about decomposition of the complexes mentioned above, and confusion of calcination conditions (flowing Ar gas was needed [2] or was not needed [3], at 450, 550 or 650 °C) appeared in different patents. In addition, it is not clear how the other two complexes in $MgCl_2{\cdot}6NH_3$ affect the quality of anhydrous $MgCl_2$ produced thereby. So it is commercially and academically significant to study the process of the decomposition of the ammoniates.

In this work, by DTA and TG analysis coupled with XRD and chemical analysis, we investigated the thermal decomposition of $MgCl_2$ hexammoniate and $MgCl_2$ biglycollate biammoniate prepared according to the USA patent [3], and the possible pathways of the decomposition of the ammoniates were discussed.

2. Experimental

Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), ethylene glycol ($C_2H_4(OH)_2$), methanol (CH_3OH), ammonia (NH_3) were obtained from commercial sources and all the solid and liquids are AR regents.

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doi:10.1016/j.tca.2003.09.018

2.1. Preparation of $MgCl_2$ hexammoniate and $MgCl_2$ biglycollate biammoniate

$MgCl_2$ hexammoniate is referred as Example 1 in Best Modes for Carrying out Invention in previous patent [3]. The preparation of $MgCl_2$ biglycollate biammoniate was obtained by a similar procedure and the difference was that the dehydrated ethylene glycol magnesium chloride solution was pumped into the reaction vessel much faster than the suggested for preparation of magnesium chloride hexammoniate, and the temperature of the vessel was maintained at about 60 °C.

2.2. Chemical analysis

Magnesium and chlorine contents were determined by ethylenediaminetetraacetic acid (EDTA) titration, the ammonia content was determined by the formaldehyde method and the methanol and glycol content by withdrawing magnesium chloride and ammonia from the total mass.

2.3. Measurement procedure

DTA and TG were recorded on SP ZRY-1P thermal analyzer at 10 °C min^{-1} heating rate and sample mass of each compound was about 5 mg in Al_2O_3 crucible. The temperature range was from room temperature to 700 °C and the thermal analyzer was calibrated with $CuSO_4 \cdot 5H_2O$.

X-ray diffraction (XRD) was carried out in D/MAX-IIIB diffractometer. The XRD powder diffractograms were recorded using the Fe Kα with 2θ angle ranging from 5° to 80°. X-ray measurements were interpreted by comparison with the database of JCPDS-International Centre for Diffraction Data.

3. Results and discussion

3.1. Characterization of the complexes

$MgCl_2$ hexammoniate formed in the procedure mentioned above was analyzed and found to contain 47.9 wt.% of magnesium chloride, 51.7 wt.% of ammonia, <1 wt.% of methanol and glycol. The mole ratio of ammonia to $MgCl_2$ is 6.1:1.0 which is in good agreement with the ratio of 6.0:1.0 expected for pure magnesium hexammoniate. XRD data of this chemical are shown in Table 1 along with the data provided in the patent [3]. XRD spectroscopy indicated an absence of $MgCl_2$ glycollate compounds.

The synthetic magnesium chloride biglycollate biammoniate was determined to contain 23.9 wt.% of magnesium chloride, 9.4 wt.% of ammonia and 66.7 wt.% of ethylene glycol, which includes both free ethylene glycol and glycol ligands of magnesium chloride glycollate compound. The ammonia and magnesium chloride contents indicated a mole ratio of ammonia to $MgCl_2$ of 2.2:1.0. XRD data of this material are shown in Table 2 with data provided in the report [3] for comparison. It could be confirmed to be magnesium chloride biglycollate biammoniate with a little of $MgCl_2$ hexammoniate.

Table 1
XRD spectrum of $MgCl_2$ hexammoniate

This work		Reference	
d (Å)	Intensity	*d* (Å)	Intensity
5.89	79	5.82	100
		5.05	3
3.605	49	3.58	60
3.071	4	3.06	6
2.943	100	2.93	85
2.547	40	2.54	40
2.27	3	2.27	3
2.079	11	2.07	20
1.961	7	1.96	6
1.802	12	1.798	12
1.722	5	1.719	4
		1.694	2
1.611	4	1.609	5
		1.469	2
1.362	3	1.360	3

3.2. Thermal decomposition of magnesium chloride hexammoniate

The DTA and TG curves of magnesium chloride hexammonia are shown in Fig. 1, and the thermal decomposition

Table 2
XRD spectrum of $MgCl_2$ biglycollate biammoniate

This work		Reference	
d (Å)	Intensity	*d* (Å)	Intensity
6.867	100	6.94	100
5.87[a]	9		
		5.44	4
		4.87	8
4.191	3	4.23	5
3.943	4	3.97	8
3.865	8	3.88	10
3.567	7	3.57	5
3.438	77	3.45	65
3.39	20	3.40	30
3.253	8	3.26	10
2.935[a]	6		
2.841	3	2.84	5
2.378	12	2.73	20
2.466	8	2.46	12
2.304	4	2.30	10
2.15	3	2.15	8
2.071[a]	4		
2.009	6	2.01	10
1.88	3	1.88	8
1.73	5	1.73	10
1.58	3	1.58	8

[a] XRD signals of $MgCl_2 \cdot 6NH_3$.

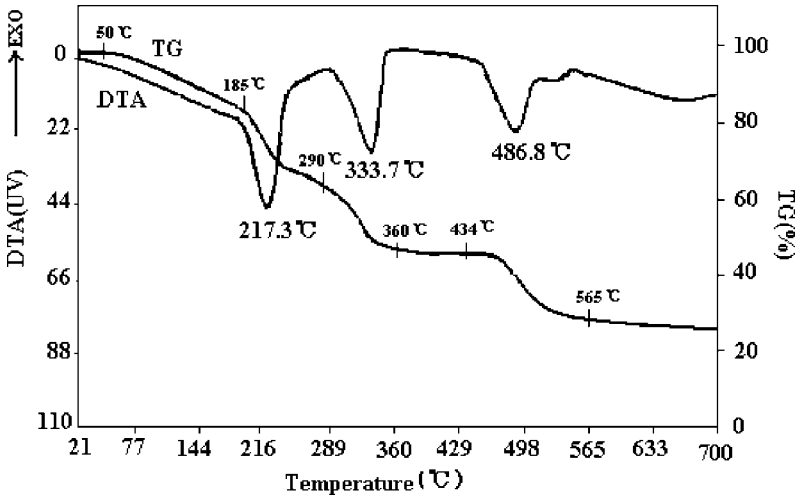

Fig. 1. DTA and TG curves of $MgCl_2{\cdot}6NH_3$.

Table 3
Thermal decomposition data for magnesium chloride hexammoniate

Step number	Temperature range (°C)	Thermal effects	Reactions	Residue (%)	
				TG	Calculated
1	50–180	Endo	$MgCl_2 \cdot 6NH_3 \rightarrow MgCl_2 \cdot 4NH_3 + 2NH_3$	82	82.8
2	180–290	Endo	$MgCl_2 \cdot 4NH_3 \rightarrow MgCl_2 \cdot 2NH_3 + 2NH_3$	65	65.5
3	290–360	Endo	$MgCl_2 \cdot 2NH_3 \rightarrow MgCl_2 + 2NH_3$	49	48.3
4	434–565	Endo	$MgCl_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \rightarrow MgO + HCl + \frac{1}{2}Cl_2$	26	20

data are given in Table 3. The chemical analyses of products of each step of the decomposition are shown in Table 4.

Four steps of the decomposition of the complex are observed with corresponding mass losses in the same ranges of temperature. No endothermal peak in the first step demonstrates that the two NH_3 have a weak bonding with Mg but $MgCl_2{\cdot}4NH_3$ is thermally stable below 180 °C. Lastra [5] in his study of equilibrium of magnesium chloride compounds with ammonia atmosphere provided the evidence of the existence of the tetrammonia of magnesium chloride, which was thought not to exist previously. TG analysis shows that there is no clear boundary between the $MgCl_2$ tetrammoniate decomposing to biammoniate and the later to anhydrous $MgCl_2$. Because of the existence of monoammoniate of magnesium chloride confirmed by previous investigation [5], the third step should contain two processes, e.g. $MgCl_2{\cdot}2NH_3$ to $MgCl_2{\cdot}NH_3$ and the later to anhydrous magnesium chloride. The fourth step should be ascribed to the oxidation of anhydrous of $MgCl_2$ to MgO. The oxidation of $MgCl_2$ in O_2 investigated by Epstein et al. [6] and Khomenko [7] indicated that Cl_2, HCl and MgO were obtained in the oxidation with the participation of H_2O. The reaction can be expressed as

$$4MgCl_2 + O_2 + 2H_2O \rightarrow 4MgO + 4HCl + 2Cl_2$$

We calculated the thermodynamic parameters of the reaction as $\Delta H^\circ_{298} = 275.06\,kJ\,mol^{-1}$ and $\Delta S^\circ_{298} = 380.3\,J\,K^{-1}\,mol^{-1}$ with the thermodynamic data of relevant substances coming from handbook [8]. It is demonstrated that the reaction is endothermal and it can only take place when the temperature is higher than 450 °C because ΔG°_{298} turns to negative since then. The calculation supports the identification of the step.

XRD measurements show that the products of the first three steps are all amorphous, and MgO was checked after the fourth step with a poor crystal.

In conclusion, thermal decomposition of $MgCl_2{\cdot}6NH_3$ contains four steps. Anhydrous $MgCl_2$ can be obtained at about 450 °C, and this is consistent with the study reported [3]. For industrial manufacture, higher temperature may be needed, so inert gas like Ar or N_2 must be used to prevent oxidation of $MgCl_2$.

Table 4
Chemical analysis of residues of $MgCl_2{\cdot}6NH_3$ and $MgCl_2{\cdot}2NH_3{\cdot}2C_2H_6O_2$ in different steps

$MgCl_2{\cdot}6NH_3$			$MgCl_2{\cdot}2NH_3{\cdot}2C_2H_6O_2$		
Step	2Cl/Mg	Residues	Step	Cl/Mg	Residues
1 + 2	1.026	$MgCl_2{\cdot}2NH_3$	1	1.042	$MgCl_2{\cdot}2NH_3{\cdot}2C_2H_6O_2$
3	0.993	$MgCl_2$	2 + 3	0.543	Mg(OH)Cl
4	0.086	$MgO + MgCl_2$	4	0.011	MgO

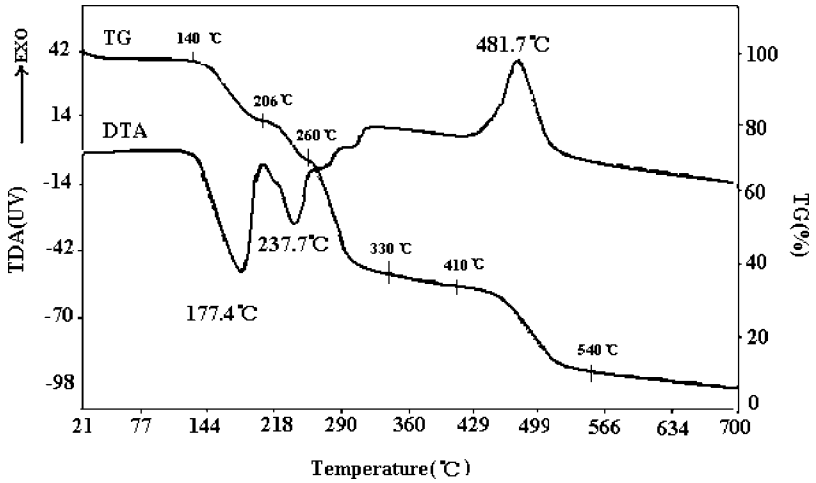

Fig. 2. DTA and TG curves of $MgCl_2{\cdot}2C_2H_6O_2{\cdot}2NH_3$.

Table 5
Thermal decomposition data for magnesium chloride biglycollate biammoniate

Step number	Temperature range (°C)	Thermal effects	Process	Residue (%)	
				TG	Calculated
1	140–206	Endo	Releasing free glycol	83	81.6
2	206–260	Endo	Releasing ammonia	70	72.2
3	260–330	Endo	Obtaining Mg(OH)Cl and C	36	35.1
4	410–540	Exo	Obtaining MgO	10	8.3

3.3. Thermal decomposition of magnesium chloride biammonia biglycol

DTA and TG curves of the decomposition of magnesium chloride biglycollate biammoniate are shown in Fig. 2, the chemical analysis results of the composition of the products of the chemical in each step are shown in Table 4 and the data of its thermal decomposition in Table 5.

From the thermal analysis, it is clear that the decomposition of magnesium chloride biglycollate biammoniate is much more complicated than the magnesium chloride hexammoniate. There are four endothermal peaks and one exothermal peak in the process of the thermal decomposition of the complex, accompanied by four mass loss steps. The first step (140–206 °C) is attributed to releasing of free ethylene glycol by the observation of no difference appearing between the residue and the original material in XRD diagram and the chemical analysis by which the composition of product of the step is identified to be glycol:ammonia:$MgCl_2$ as 2.1:1.9:1.0. The second step (206–260 °C) may be removal of two molecules of ammonia from the complex, the next step which corresponds to the third (260–330 °C) endothermal peaks obtains Mg(OH)Cl and C identified by XRD and the black color of the product. The last step (410–540 °C), corresponding to the exothermal peak, is easily assigned to the reaction of C burning in air. XRD measurement of the residue indicates that MgO was formed in the step, which may be a process of decomposition of Mg(OH)Cl but at a lower temperature than in the previous one [9].

About the formation of carbon, we hypothesize the following mechanism:

$$MgCl_2 \cdot 2C_2H_6O_2 \cdot 2NH_3 \xrightarrow{273\,^\circ C} MgCl_2 \cdot 2C_2H_6O_2 + 2NH_3 \uparrow$$

$$MgCl_2 \cdot 2C_2H_6O_2 \xrightarrow{270\,^\circ C} MgCl_2 + 2OH\text{–}CH_2\text{–}CH_2\text{–}OH$$

$$MgCl_2 + H_2O \xrightarrow{300\,^\circ C} Mg(OH)Cl + HCl$$

$$OH\text{–}CH_2\text{–}CH_2\text{–}OH + O_2 \xrightarrow{300\,^\circ C} C + 4H_2O$$

In conclusion, the formation of Mg(OH)Cl and carbon in the decomposition of $MgCl_2{\cdot}2C_2H_6O_2{\cdot}2NH_3$ indicates that this complex is useless for the production of anhydrous magnesium chloride, and its formation when precipitating $MgCl_2{\cdot}6NH_3$ in anhydrous magnesium chloride–ethylene glycol solution with a poor condition control will define the quality and appearance of anhydrous $MgCl_2$ product.

4. Conclusion

From this work, we concluded that anhydrous $MgCl_2$ can be produced by the decomposition of $MgCl_2$ hexam-

moniate at 450 °C or higher temperature in inert gas atmosphere. When manufacturing $MgCl_2$ hexammoniate in the $C_2H_4(OH)_2$, the condition must be carefully controlled to decrease the formation of $MgCl_2{\cdot}2C_2H_6O_2$ as little as possible.

Acknowledgements

This research was supported by the Chinese Academy of Science under XIBU ZHI GUANG program.

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