Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 61–65

THERMAL DECOMPOSITION OF MANGANESE(II)BIS(OXALATO)NICKELATE(II)TETRAHYDRATE

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A mixed metal oxalate, manganese(II)bis(oxalato)nickelate(II)tetrahydrate, has been synthesized and characterized by elemental analysis, IR spectral and X-ray powder diffraction (XRD) studies. Thermal decomposition studies (TG, DTG and DTA) in air showed that the compound decomposed mainly to Mn_2O_3, MnO_2 and NiO at ca.1000°C, via. the formation of several intermediates. DSC study in nitrogen upto 500°C showed the endothermic decomposition. The tentative mechanism for the thermal decomposition in air is proposed.

Keywords: *IR, oxalato, thermal decomposition, X-ray powder diffraction*

Introduction

Thermal decomposition of co-precipitated zinc-copper oxalates in nitrogen indicated [1] the formation of mixed oxide and copper metal as end product. The structure and magnetic properties of $NiCu(C_2O_4)_2 \cdot 4H_2O$ have been studied [2]. The oxalates of mixed metal of barium [3] and lead [4] with titanium of the type $BaTiO(C_2O_4)_2$ and $PbTiO(C_2O_4)_2 \cdot 4H_2O$ are reported. We have synthesized and investigated [5, 6] the thermal decomposition of the compounds, $M[M(C_2O_4)_2] \cdot xH_2O$ (where, M = same metal) with Mn and Ni in air and nitrogen. The alkali metal uranyl oxalate of the type, $M_2UO_2(C_2O_4)_2 \cdot xH_2O$ (M=Li, Na) [7] were found to decompose to monouranates around 800°C through the formation of alkali metal carbonates and UO_2 as intermediates at ~400°C. Mixed metal oxalates of lanthanides and uranium of the type $(NH_4)Ln^{III}U^{IV}(C_2O_4)_4 \cdot 8H_2O$ (Ln=La, Ce, Pr, Nd, Tb) [8] were indexed on an orthorhombic unit cell. The compounds were decomposed to $Ln_2O_2CO_3$ and UO_{2+x} as intermediate products in the range 625 to 655 K. Further above 975 K the intermediates formed solid solutions of mixed oxides with fluorite structure in air, argon and N_2/H_2. The thermal decomposition behaviour of thallium(I)bis-oxalatodiaquaindate(III)-monohydrate and barium dioxodiaquaperoxyoxalatouranate was studied and their structural formulas were proposed as $Tl[In(C_2O_4)_2(H_2O)_2] \cdot H_2O$ [9] and $Ba[UO_2(O_2)(C_2O_4)(H_2O)_2] \cdot H_2O$ [10]. The dehydration/rehydration of ammonium tris-oxalato aluminate(III), $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ was studied [11] in flowing dinitrogen saturated with water vapour at room temperature. Recently, we reported the thermal investigation of the compounds, $M[Ni(C_2O_4)_2] \cdot xH_2O$ (M=Co(II) or Cd(II)) [12], $M[La(C_2O_4)_3] \cdot xH_2O$ (M=Cr(III) or Co(III) [13], $Zn[Co(C_2O_4)_2] \cdot 5H_2O$ [14] and $Cd[Co(C_2O_4)_2] \cdot 5H_2O$ [15]. Although, there have been quite a few reports on the mixed metal oxalate, so far oxalate of manganese with nickel of the type $M[M(C_2O_4)_2] \cdot xH_2O$ (where, M=different metal) has not been reported. As an extension of our work on mixed metal oxalate, and, keeping in view of the possibility of formation of different types of metal oxide and mixed metal oxides and their possible applicability as prospective materials for superior technical ceramics, magnetic recording materials, electronic components, catalysts as well as high-temperature superconductors, this paper describes the synthesis, characterization and thermal decomposition behaviour in solid state of $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$ in air. A tentative route of the decomposition in air is also proposed.

Experimental

The preparative method is similar to the method adopted earlier [12–15]. The chloride free nickel hydroxide prepared from nickel chloride was dissolved in glacial acetic acid and heated on a steam bath. A light blue precipitate was separated on adding a solution of manganese chloride followed by dropwise addition of saturated solution of oxalic acid. The precipitate was filtered off, washed several times with distilled water and stored in a desiccator over calcium

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1388–6150/$20.00

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chloride. The water content was determined gravimetrically and thermogravimetrically. The manganese and nickel content were estimated gravimetrically by precipitating as $MnNH_4PO_4 \cdot H_2O$ and bis(dimethylglyoximato)nickel(II) respectively. Carbon and hydrogen contents were analyzed using a Carlo Erba 1108 elemental analyser. Analysis as calculated for $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$: Mn 14.47%; Ni 15.46%; C 12.65%; H 2.65%; H_2O 23.72%; found: Mn 14.23%; Ni 15.06%; C 12.17%; H 2.60%; H_2O 22.65%

IR spectra (200–4000 cm^{-1}) and powder X-ray diffraction (XRD) pattern were carried out as described earlier [12, 16, 17]. TG, DTG and DTA curves were recorded in static air up to 1000°C at a heating rate of 10°C min^{-1} using a Shimadzu DT 30B thermal analyser. The intermediate phases and end products were isolated by independent pyrolysis in air upto the required temperature in furnace. Sometimes these were isolated by temperature arrest technique (stopping of the TG scan) upto the required temperature in TG. DSC curve was recorded with a TA instrument DSC-2010 at a heating rate of 10°C min^{-1} in nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The instrument was calibrated with indium (purity 99.9%). The enthalpy (ΔH) values are obtained through universal V2.3C TA software in J g^{-1} and converted into kJ mol^{-1} using molecular mass, and entropies (ΔS) are calculated using simple well known thermodynamic relation incorporating the temperature of peak maxima.

Results and discussion

The complex, $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$ was insoluble in water and common organic solvents, but it decomposes in the presence of strong acid and alkali. Analytical and microanalytical results suggest the proposed formula of the compound. Selected bands (Table 1) in the IR spectrum of the compound suggested [12–18] the chelating character of the oxalato groups and the XRD patterns (Table 2) suggest the crystalline nature.

Table 1 Selected bands in the IR spectrum of $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$

IR bands[a] /cm^{-1}	Assignments
3000–3800 Sb	$\nu_{sy}(O–H)+\nu_{asy}(O–H)$ or hydrogen bonding
1630 S	$\delta_{sy}(H–O–H)$
1500–1800 Sb	$\nu_{asy}(C=O)$
1370 m	$\nu_{sy}(C–O)$ and / or $\nu(C–C)$
1320 m	$\nu_{sy}(C–O)$ and / or $\delta(O–C=O)$
730 s, 820 m	$\nu(M–O)$ and / or $\delta(O–C=O)$ or coordinated water
610 s	water of crystallization
460 m	$\delta(O–C=O)$ and / or ring deformation
290 s	π (out-of-plane bending)

[a] s=small, m =medium, S=strong, b=broad

Table 2 X-ray powder diffraction data of $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$

$Mn[Ni(C_2O_4)_2] \cdot 4H_2O$	
d/Å	*I*/Rel
8.013	49.38
4.772	100.00
3.632	65.37
2.986	71.86
2.656	68.71
2.262	58.63
1.914	62.72
1.626	63.33
1.475	59.64
1.363	61.97
1.264	63.93
1.175	66.62
1.103	64.94
1.006	69.91
0.961	75.75
0.939	76.27
0.902	78.01
0.875	75.38
0.820	81.69
0.809	80.53

The thermal profiles (TG, DTG and DTA) of $Mn[Ni(C_2O_4)_2] \cdot 4H_2O$ in air is seen in Fig. 1. An inclined slope in TG profile between 147 and 225°C with mass loss of 19% (calculated, 19.92%) indicates the formation of anhydrous species. A sharp change in DTG between 138 and 238°C, and an endothermic peak in DTA between 130 and 232°C (ΔT_{min}=182°C) correspond to the dehydration step. The pyrolysed product in air at 272°C shows the IR bands at 1420–1900, 1360, 1310, 820, 720, 460 and ca. 280 cm^{-1} indicates the presence of chelating oxalato groups; however, the XRD data (Table 3) are not similar to the parent compound. The removal of water at higher temperature suggests the presence of coordinated water. The anhydrous species is stable upto 305°C. Further, a steep slope in TG curve upto 354°C with mass loss of 54% apparently indicates the formation of $NiMnO_3$ (calculated mass loss, 55.32%) which is an intimate mixture of NiO and MnO_2. But there is less possibility of formation of $NiMnO_3$ at this temperature, because solid-solid reaction of molten

Table 3 X-ray powder diffraction data of the pyrolysed products of $Mn[Ni(C_2O_4)_2]\cdot 4H_2O$ at 272, 380, 770 and 1000°C

Pyrolysed product at							
272°C		380°C		770°C		1000°C	
d/Å	*I*/Rel	*d*/Å	*I*/Rel	*d*/Å	*I*/Rel	*d*/Å	*I*/Rel
8.453	37.26	6.365	79.68	7.942	66.62	6.041	77.63
4.779	54.36	3.385	79.32	4.544	71.22	3.902	82.52
3.382	48.15	3.026	84.97	3.767	68.94	▪2.724	100.00
3.071	47.92	⊗2.973	82.92	♦3.094	78.32	#▲1.666	66.48
2.591	53.26	▲2.540	100.00	3.035	80.12	▲1.352	59.68
1.849	54.49	*△□2.079	83.15	▲*•2.565	100.00	⊗▲1.273	63.52
1.353	52.39	▲1.626	83.17	▪2.113	75.67	▪1.177	61.97
1.186	58.44	*▲1.548	84.98	▪1.851	75.23	⊗□1.048	57.69
1.058	64.33	▲1.361	79.26	▲*1.703	73.03	1.013	56.58
0.984	65.32	⊗ ▲1.213	79.67	♦▪1.495	80.68	□0.958	50.79
0.948	69.98	*1.160	82.12	o1.406	70.76	□0.929	55.25
0.916	75.44	△1.152	80.80	▲♦1.291	73.70	▽0.886	52.03
0.895	75.28	⊗1.090	77.21	▪1.184	73.89	□ •0.853	54.98
0.880	80.78	*△1.082	75.10	▪♦o1.105	80.37	0.834	58.25
0.862	78.14	*△1.017	75.03	•1.010	78.93	0.819	58.37
0.833	90.49	△0.966	73.76	□0.963	76.83	▽□0.806	56.11
0.816	92.91	□0.958	78.26	□0.934	77.93	0.800	61.08
0.799	93.33	0.939	80.09	0.917	75.41	•0.786	60.16
0.793	100.00	□0.934	82.28	▽0.887	77.92		
		•0.908	75.60	•0.858	80.17		
		▽0.885	79.78	0.833	83.41		
		•0.862	80.83	▽0.812	78.54		
		0.829	75.96	□0.796	79.02		
		▽0.814	79.55				
		□0.799	78.76				
		•0.786	79.61				

♦– Mn_3O_4; ▪ – Mn_2O_3; ▲-MnO_2; • – MnO; △ – $NiCO_3$; □ – NiO; o – Ni_2O_3; ▽ – NiC; * – C; # – $NiMnO_3$; ⊗$NiMn_2O_4$

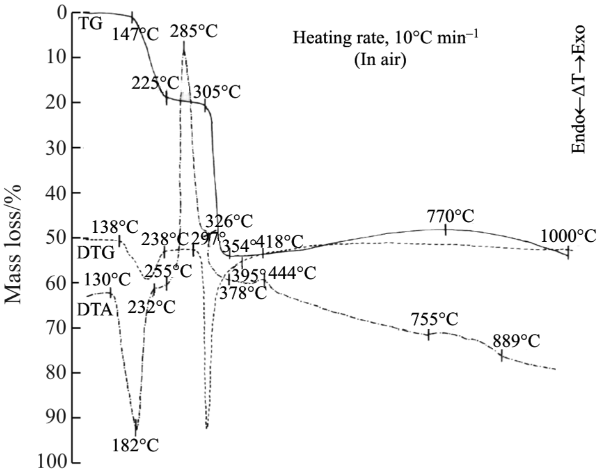

Fig. 1 TG, DTG and DTA curves of $Mn[Ni(C_2O_4)_2]\cdot 4H_2O$ in air at 10°C min^{-1}

NiO and MnO_2 only at high temperature produces the mixed metal oxides. A strong exotherm in the range 255–378°C (ΔT_{max} = 285°C) with a shoulder at 326°C in DTA and a sharp DTG change between 297 to 395°C are accounted for this decomposition step. The black pyrolysed species in air at 380°C shows the IR bands at 1380, 1350, 610, 550, 460, 400, 330, 310 and 240 $cm^{-1,}$ which indicated the presence of MnO_2 and NiO [19]. The XRD data (Table 3) of the species confirmed [20] the compound to be a mixture of NiO and MnO_2. Although, the peaks for $NiMnO_3$ are not obtained, however, the presence of a trace of MnO is confirmed from XRD data. A few d-values are coincides with $NiMn_2O_4$, indicates its presence which is simply a mixture of NiO and Mn_2O_3. So in this study it is apparently indicated that at 354°C, a part of MnO_2 and MnO combined, which, inturn formed Mn_2O_3 (which immediately reacted with a part of

NiO, forming $Ni^{II}Mn_2^{III}O_4$) with the change of the oxidation state from Mn^{IV} and Mn^{II} to Mn^{III}. A shoulder at 326°C in DTA may be due to these changes of state in manganese or combination of NiO and Mn_2O_3. The evolved CO (g) is responsible to reduce Mn^{IV} to Mn^{III} and simultaneous air oxidation of Mn^{II} to Mn^{III} cannot be ruled out. The presence of $NiCO_3$, C (carbon) and trace of NiC are confirmed from the XRD data (Table 3); the formation of NiC is possible at this temperature as a part of NiO reacts with C which formed through disproportionation of CO (g) to CO_2 (g). The extra band in the IR spectrum of the species isolated at 380°C may be due to the presence of trace of the carbides, carbonates and mixed metal oxides. The TG curve is stable upto 418°C and then slow increase of mass of 6% upto 770°C (mass loss, calcd., 48%) and then again decreases slowly upto 1000°C with a mass loss of 54% indicates the formation of compound similar to the species formed at 354°C in TG. The XRD data (Table 3) of the black pyrolysed product at 770°C in air confirmed the presence of Mn_3O_4, Mn_2O_3, MnO_2, MnO (trace), NiO/Ni_2O_3 and NiC (trace). A very small exothermal hump in DTA at 444°C may corresponds to the oxidation of MnO to Mn_2O_3 and Mn_3O_4 (the later also might have generated from the interaction of MnO & Mn_2O_3 at this temperature), NiO to Ni_2O_3 or may be due to the slow decomposition of $NiMn_2O_4$ (trace) at high temperature again to NiO and Mn_2O_3. In TG the 6% weight gain in the range 418° to 770°C supports these oxidation. The black pyrolysed product at 770°C in air shows the IR bands at 1380, 1350, 600, 540, 440, 400, 310 and 240 cm^{-1} that shows the presence of the oxides of manganese and nickel. Further, a slight exothermal nature of DTA curve in the range 755-889°C may be due to the changes of the products formed at 770°C in TG. The pyrolysed grey species at 1000°C in air is found to be a mixture of Mn_2O_3, MnO_2 and NiO as confirmed [20] from the XRD data (Table 3). A trace of $NiMnO_3$ and again $NiMn_2O_4$ are also detected from XRD which may be formed from the solid-solid reaction of a part of molten NiO with MnO_2 (molten) and Mn_2O_3 (molten) respectively at this high temperature. The exothermal nature of DTA (755 – 889°C) may be due to change of Mn_3O_4 to Mn_2O_3. The presence of trace of MnO and NiC cannot be ruled out as identified from XRD. The IR bands of the species isolated at 1000°C supports the presence of the oxides of manganese and nickel.

The DSC profile (Fig. 2) in nitrogen upto 500°C shows two sharp endothermic changes. The first endotherm in the range 125–257°C corresponds to the dehydration. The enthalpy (ΔH) and entropy changes (ΔS) of the step are found to be 216.83 kJ mol^{-1} and 461.53 J K^{-1} mol^{-1} respectively. The second endotherm between 325 and 460°C manifests to the decomposition and the respective values of ΔH and ΔS are calculated to be 146.43 kJ mol^{-1} and 208.95 J K^{-1} mol^{-1}.

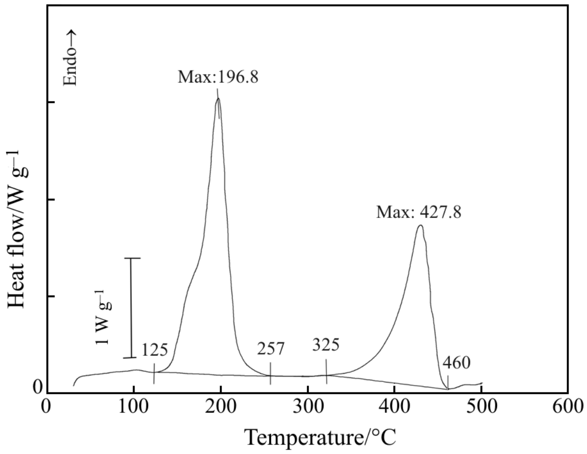

Fig. 2 DSC profile of $Mn[Ni(C_2O_4)_2]\cdot 4H_2O$ in nitrogen at 10°C min^{-1}

The foregoing results suggest the following tentative decomposition scheme in air.

$$
\begin{gathered}
Mn[Ni(C_2O_4)_2]\cdot 4H_2O \xrightarrow{ca.225°C} Mn[Ni(C_2O_4)_2]\ (s) + \\
4H_2O\ (v) \xrightarrow{305–354°C} MnO_2\ (s) + MnO\ (s)(trace) + \\
NiO\ (s) + NiCO_3\ (s) + NiC\ (s)(trace) + C\ (s) + \\
lCO(g) + mCO_2\ (g) \xrightarrow{ca.770°C} Mn_3O_4\ (s) + \\
Mn_2O_3\ (s) + MnO_2\ (s)(unreacted) + \\
MnO\ (s)(trace) + [NiO + Ni_2O_3]\ (s)(trace) + \\
NiC\ (s)(trace) + xCO_2(g) \xrightarrow{ca.1000°C} Mn_2O_3\ (s) + \\
MnO_2\ (s) + NiO\ (s) + MnO\ (s)(trace) + \\
NiC\ (s)(trace)
\end{gathered}
$$

Acknowledgements

The author is thankful to Dr.S.D.Baruah, Regional Research Laboratory, Jorhat for the DSC profile and Director, RSIC, CDRI, Lucknow for elemental analysis.

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Received: September 18, 2004
In revised form: January 22, 2005

DOI: 10.1007/s10973-005-6493-2