Thermochimica Acta, 89 (1985) 391–394
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMAL DECOMPOSITION OF COPPER(II), NICKEL(II), COBALT(II) AND IRON(II) OXALATES IN SELF-GENERATED ATMOSPHERES

E.A. GUSEV, S.V. DALIDOVICH, V.A. SHANDAKOV and A.A. VECHER

Byelorussian State University, 220080 Minsk (U.S.S.R.)

(Received 31 January 1985)

At present there are a great number of works dealing with investigations of the reactions of decomposition of bivalent nickel, cobalt, iron and copper oxalates both under isothermal and non-isothermal conditions. An extended bibliography on this is given in ref. 1. However, the literature does not provide any data concerning investigations of these substances under isochoric conditions. Few works exist [2,3] dealing with studies of the pyrolysis of substances in their own gaseous product atmosphere. In this paper we use a technique of studying decomposition reactions in sealed ampoules which allows more reliable quantitative data to be obtained on decomposition enthalpies of substances accompanied by gassing, since in this case there are no heat or mass exchanges of samples and their decomposition products with the environment. This is mentioned in ref. 3 when studying the dehydration reactions of nickel salts. Such a technique, to a great extent, also allows the influence of the gaseous products on the decomposition of the basic substance and their interaction to be clarified.

EXPERIMENTAL

Crystallohydrates of nickel, cobalt and iron oxalates were of reagent grade. Copper oxalate was synthesized by means of a conventional method and it contained about 0.3 moles of absorbed H_2O per 1 mole of salt.

Thermal analysis was conducted using a dynamic triple-heat-bridge calorimeter [4]. Special stainless-steel ampoules were used of 0.9 cm^3 volume. These ampoules resisted pressure up to 10 MPa. Before sealing, the ampoules with samples were filled with Ar. The heating rate of the ampoules was 2 K min^{-1}. The temperature range of the investigations was 150–700 K and the sample weight used was 28–32 mg. After the decomposition of the samples the ampoules were cooled down to 100 K without being removed from the calorimeter cell and then they were reheated. Amounts of CO_2 and H_2O in the decomposition products were determined according to the peaks corre-

0040-6031/85/$03.30

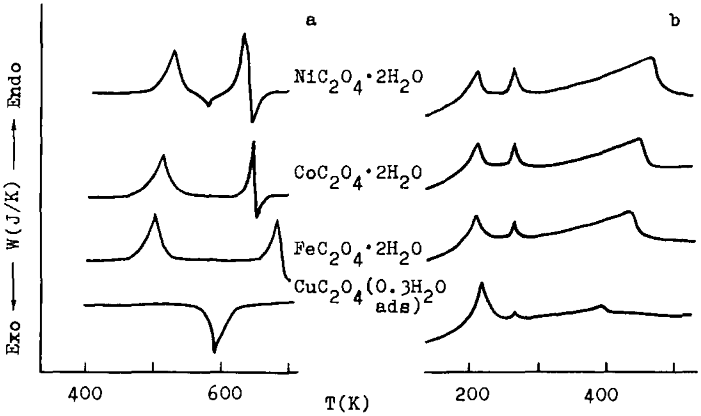

Fig. 1. Thermal curves of the decomposition of oxalates in sealed ampoules: (a) initial substances; (b) products of their decomposition.

sponding to CO_2 sublimation and H_2O melting and vaporization. After reheating the ampoules were opened and the quantity of gaseous products was determined. The composition of the gaseous products was analysed by means of a MAT-311 mass spectrometer. Solid products of the decomposition reactions were analysed by the X-ray method.

RESULTS AND DISCUSSION

Results of the thermal analysis of the samples and the complex investigation of their pyrolysis products are shown in Fig. 1 and summarized in Table 1. From these data it follows that Ni, Co and Fe oxalates decompose

TABLE 1

Results of thermal analysis of oxalates under isochoric conditions

Sample	$NiC_2O_4 \cdot 2H_2O$	$CoC_2O_4 \cdot 2H_2O$	$FeC_2O_4 \cdot 2H_2O$	CuC_2O_4 ($0.3H_2O$(ads))
Dehydration temp. (K)	490–560	460–540	460–540	–
Hydration enthalpy (kJ mol^{-1})	91 ± 5	90 ± 5	94 ± 5	–
Decomposition temp. (K)	600–670	610–680	630–700	560–630
Decomposition enthalpy (kJ mol^{-1})	32 ± 2	30 ± 2	–	−29 ± 2
Gaseous products	H_2, H_2O, CO, CO_2	H_2, H_2O, CO, CO_2	H_2, H_2O, CO, CO_2	H_2, H_2O, CO, CO_2
Solid products	Ni, NiO	Co_2O_3	Fe_2O_3	Cu, Cu_2O
Dehydration temp. in air (K)	450–510	430–480	450–490	–
Decomposition temp. in air (K)	640–680	630–690	630–730	600–630

practically in the same way. As it was to be expected, the temperature ranges of dehydration in the ampoules were shifted 50–60 K higher in comparison with dehydration in air. Dehydration enthalpies of the samples are close to each other and are, approximately, $\Delta H_v = 92 \pm 5$ kJ mol^{-1} (recalculation for ΔH_p gives the value 100 ± 5 kJ mol^{-1}). The values obtained agree well with those on the activation energy of the dehydration process given in ref. 1. Thus, one can suppose that the dehydration reactions of Ni, Co and Fe oxalates are "normal" (when $E \approx \Delta H$) and satisfy the Polanyi–Wigner equation.

On the contrary, the decomposition temperature intervals of the anhydrated salts during the experiment are shifted, on average, 30–50 K lower in comparison with decomposition in air. As it follows from analyses of the shapes of the curves obtained and gaseous and solid products, the decomposition mechanism is a complex one and the decomposition process consists of a number of simultaneous, parallel reactions. This is confirmed by the sharp transition from the initial stages, accompanied by heat absorption, to a stage accompanied by heat evolution. Evidently, the main role here belongs not only to the catalytic activity of the metal being formed, but also to possible reactions of this metal with CO_2. This is proved by the reduced quantity of CO_2 in comparison with that which, theoretically, should have been formed during the metal oxalate decomposition. It was also stated that the reaction of CO with H_2O vapour takes place during the experiments. As it is known this reaction is greatly accelerated in the presence of the solid decomposition products (metal, metal oxide).

Unlike the metal oxalates discussed above, Cu oxalate decomposes in one stage (Fig. 1) proceeding with the evolution of heat. Adsorbed water contained in the sample had an influence on the composition of the final decomposition products.

Due to the impossibility of conducting investigations above 700 K the thermal curve of Fe oxalate was only partially obtained.

On the basis of the data obtained one can make the conclusion that decomposition reactions of the metal oxalates studied in self-generated atmospheres are expressed by the following equations

$$2FeC_2O_4 \cdot 2H_2O = Fe_2O_3 + 2H_2O + 3CO_2 + CO + 2H_2$$

$$2CoC_2O_4 \cdot 2H_2O = Co_2O_3 + 2.5H_2O + 2.5CO_2 + 1.5CO + 1.5H_2$$

$$2NiC_2O_4 \cdot 2H_2O = 0.2Ni + 1.8NiO + 3.6H_2O + 2.6CO_2 + 1.4CO + 0.4H_2$$

$$2CuC_2O_4(0.3H_2O(ads)) = Cu + 0.5Cu_2O + 0.3H_2O + 3.8CO_2 + 0.2CO + 0.3H_2$$

REFERENCES

1 M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State (translated from English), Mir, Moscow, 1983.
2 P.D. Garn, Anal. Chem., 37 (1965) 77.
3 W.W. Wendlandt, Thermochim. Acta, 9 (1974) 101.
4 A.A. Vechler, A.G. Gusakov and A.A. Kozyro, Russ. J. Phys. Chem., 53 (1979) 783.