

Short Communication

THERMAL DECOMPOSITION OF MIXED OXALATES

PART I: THERMOGRAVIMETRIC ANALYSIS OF COPRECIPITATED ZINC-COPPER OXALATES IN NITROGEN

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(Received February 8, 1978)

The thermogravimetric analysis of several coprecipitated zinc-copper oxalates in nitrogen is reported. The thermal decompositions of these mixed oxalates show a separate single step for dehydration and decomposition in the mass loss versus temperature curve. It is found that the onset temperature decreases with composition. For example, it decreases from 380° for zinc oxalate to 260° for copper oxalate. The end-product is mixed oxides and copper metal. These studies indicate the formation of an interpenetrating structure or mixed crystals during coprecipitation. Rate parameters have been calculated for dehydration and decomposition.

The purpose of the present investigation was to study the effect of coprecipitated copper oxalate on the decomposition temperature of zinc oxalate in nitrogen with a view to elucidating the nature of these materials.

Material and method

Mixed oxalates of zinc and copper were prepared by a coprecipitation method. The copper and zinc contents of the mixed oxalates were determined by conventional chemical methods. The compositions showed some deviation from the proportions of the two salt solutions taken.

The dehydration and decomposition temperatures of these mixed oxalates in nitrogen were determined in a thermogravimetric balance using a McBain-Baker type quartz spring [1]. This had a sensitivity of 5.6 mg/mm extension and required only about 25 mg of sample for investigation. The extension of the spring was measured with a travelling microscope every 2 min, while the temperature of the furnace was increased at a constant rate of about 5°/min by means of a programming system described separately. The thermal analysis was carried out in flowing nitrogen gas, which was purified by passage through alkaline pyrogallol solution followed by moisture traps (a calcium chloride tower and silica gel drying tube).

Results and discussion

Dehydration and decomposition temperatures reproducible within $\pm 1.5^\circ$ were obtained. The results were plotted as percent weight loss against temperature. The plots of four representative oxalates are shown in Fig. 1. The first part of the

thermal curve corresponds to the dehydration step and the second part represents the decomposition. Generally the shape of the curves remains the same, except for a lowering of the onset dehydration and decomposition temperature. The physical mixture of zinc oxalate and copper oxalate shows two distinct steps of decomposition corresponding to the two oxalates. The ranges for dehydration and decomposition temperatures and details of weight losses incurred are recorded in Table 1.

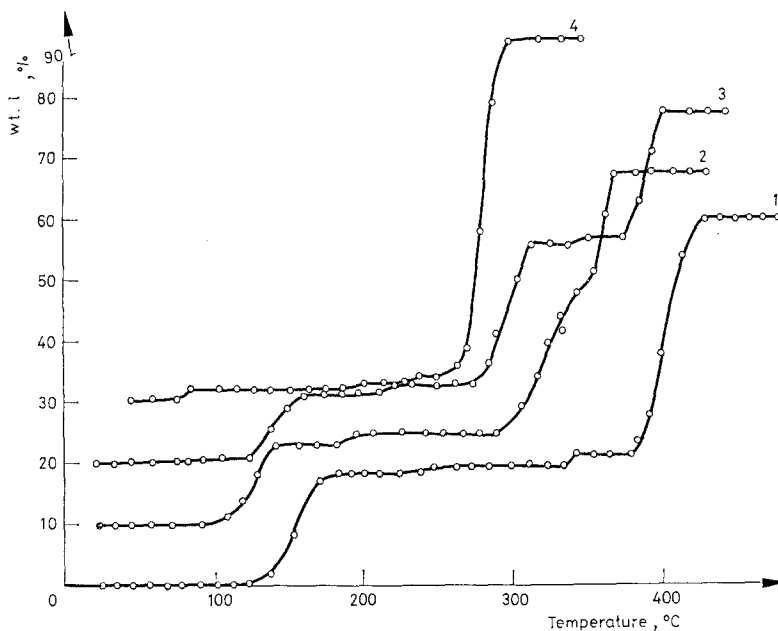


Fig. 1. TG curves of zinc oxalate, mixed 46.2% copper oxalate, physical mixture and copper oxalate in N_2 gas medium: 1. zinc oxalate, 2. mixed oxalate (46.2% copper); 3. physical mixture (50 : 50), 4. copper oxalate

The experiments show two classes of oxalate decomposition; in the first is the oxalate of zinc, which produces oxide as a result of decomposition, and in the second the oxalate of copper, whose decomposition produces metal and oxide. This is confirmed by X-ray analysis of the decomposed products of the oxalates. The coprecipitated mixed zinc-copper oxalates also showed these two classes of decomposition.

The process of thermal decomposition of these mixed oxalates can be expressed by the following general stoichiometric equation:

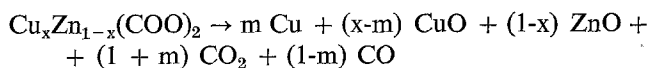


Table 1

Percentage of copper in precipitate	Dehydration step				
	Onset temp., °C	Termination temp., °C	Percentage loss		Activation energy, kcal/mole
			From graph	Calculated	
0.00	123	184	19.50	19.00	23.73
6.80	98	146	19.00	18.23	32.69
14.70	120	166	17.50	17.30	29.52
23.70	109	154	16.00	16.21	22.88
34.20	103	147	15.00	14.91	22.03
46.20	98	142	13.50	13.35	25.42
54.70	106	140	10.00	12.70	26.40
68.80	110	135	8.00	10.26	24.96
77.40	96	132	6.50	9.04	52.80
91.20	—	—	3.00	6.97	—
100.00	—	—	2.00	5.60	—

Decomposition step					
Onset temp., °C	Termination temp., °C	Percentage loss			Activation energy, kcal/mole
		From graph	Calculated assuming ZnO + CuO as end product	Calculated assuming ZnO + Cu as end product	
380	429	59.50	57.03	57.03	54.91
350	386	58.50	56.64	57.24	79.58
345	384	58.50	56.19	57.46	133.76
332	376	57.50	55.66	57.73	75.83
288	372	57.50	55.02	58.06	26.15
289	369	57.00	54.26	58.46	17.71
270	373	57.00	53.41	58.43	20.02
280	334	56.39	52.74	59.23	35.20
268	332	58.00	52.13	59.55	87.90
268	321	57.00	51.12	60.07	98.56
260	300	58.00	50.45	60.42	38.53

The observation of a single step in the thermal curves of the coprecipitated oxalates may be taken as an indication of a homogeneous phase. In view of this observation it may be expected that a double compound of the type $ZnCu(COO)_4$ may have been formed. However, significant variations in the compositions of the precipitates with changes in the proportions of the reactant zinc and copper solutions and also of their onset dehydration and decomposition temperatures (Table 1), do not appear to support the formation of any definite compound.

It may be assumed that the lowering of the decomposition temperature of the mixed oxalates is caused by the earlier initiation of the exothermic decomposition

of copper oxalate in it, the local heat thus generated being sufficient to effect decomposition of zinc oxalate as well. In such a case the onset decomposition temperature of the sample would have been the same as that of copper oxalate and the final temperature would have been comparable to that of zinc oxalate. This is contrary to our observations in that the onset decomposition temperatures of the coprecipitated oxalates are substantially higher than that of copper oxalate, and the temperatures of completion of decomposition are distinctly lower than that of zinc oxalate. These observations seem to indicate that during coprecipitation zinc and copper oxalates form an interpenetrating matrix, representing in the dry state a meta-stable solid solution at the grain boundaries.

Calculation of rate parameters

Freeman and Carroll [2] and Coats and Redfern [3] have shown that the kinetic parameters of any decomposition process could be calculated from the characteristics of the TG curve. It was found that the Freeman and Carroll relationship is not very suitable in the present case. However, the relationship of Coats and Redfern was found to be quite satisfactory for the TG curves of the mixed Zn-Cu oxalates. From the values of the activation energy for the dehydration and decomposition calculated with the help of the above relationship (Table 1), it is seen that the activation energy is not in a linear correlation with the composition of the mixed oxalates. The order of reaction, n , for dehydration and decomposition was found to be 0.66 and 0.50, respectively.

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One of us (B. D. D.) is grateful to the University Grants Commission, New Delhi, India, for the award of a research fellowship.

References

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