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The activities of some metal oxides in promoting the thermal decomposition of potassium oxalate

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Abstract

Transition metal oxalates undergo anion breakdown in the solid state, many between 200 and 400 °C, at much lower temperatures than the decomposition of potassium oxalate (at around 600 °C) which melts at about 400 °C. The present article reports studies of the chemical changes that occurred on heating equimolar crushed mixtures of potassium oxalate with each of a range of (mainly transition metal) oxides, ZnO, PbO, NiO, CuO, Cu_2O, Fe_2O_3, Co_3O_4 and Cr_2O_3, in flowing air or hydrogen. The objective was to determine the abilities of these added oxides to promote oxalate ion breakdown. Possible mechanisms of catalysis appeared to include the intervention of the relatively less stable metal oxalates and/or a heterogeneous, catalytic reaction on the surfaces of the oxide or, under reducing conditions, on some of these metals. Melting might also be expected to increase reactivity.

The results showed that the activities of these selected oxides in promoting oxalate anion breakdown were unexpectedly small. While these additives resulted in some reaction, there was evidence of the occurrence of some unpromoted decomposition of potassium oxalate during the final stages of heating (about 590–650 °C) of all the mixtures studied. Under reducing conditions, in hydrogen, the limited catalytic activities of most oxides were further diminished, evidence that the metal formed was inactive. This contrasts with the autocatalytic reactions, envisaged as proceeding on the surfaces of metal product, in some solid state decompositions, such as nickel oxalate. Potassium oxalate melting was not associated with any increase in reactivity. It is concluded that these oxides do not interact appreciably with the ionic salt and potential oxalate intermediates do not form under these conditions. Surfaces of oxides and of metals similarly do not exhibit catalytic activity for the breakdown of ionic oxalate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The solid state thermal decompositions of metal oxalates [1] have long been regarded as reactants suitable for the investigations of crystolysis reactions [2]. However, although there has been a considerable investment of effort, this has lead to little agreement in identifying the parameters controlling reactivity or the mechanisms of anion breakdown for reactions proceeding in the solid state. The several attempts that have been made to classify these thermal reactions [3] have not so far succeeded in identifying criteria whereby behaviour can be systematically ordered or in providing insights into the factors that determine and control reactivity. In literature discussions of reaction models proposed to account for the thermal decompositions of carboxylates, an unusually wide

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range of rate determining processes have been considered [1]. These include rupture of the various bonds within and between the constituent ions, electron transfer steps, catalysis by solid products and others. Thus, the behaviour of this particular group of reactants is truly representative of a field in which little recent progress has been made towards classifying crystolysis reactions of solids through chemical similarities, absolute reactivities, or reaction mechanisms [3].

A recent contribution to this unresolved problem by L'vov [4] advances a novel approach to theory development for solid state decompositions, specifically considering a selected range of oxalates for which the necessary thermodynamic data are available. This identifies the first step as the dissociative evaporation of the reactant with simultaneous condensation of the products of low volatility. The results show that, for this particular group of thermal reactions, the model is capable of accounting for the absolute reactivity and the kinetic characteristics, through known properties of the reactant. This offers a new theoretical explanation of reactions for which no general theory is currently available.

In previous studies of oxalate decompositions, we identified correlations between the activation energy for the reaction and the strength of the cation-oxygen bond [5,6]. To contribute towards understanding of the general chemistry of oxalate anion breakdown in the presence of cations, the present comparative studies were undertaken of the thermal decompositions of mixtures of potassium oxalate with selected, mainly transition metal, oxides. Interest was directed particularly towards characterising the steps that participate in the $C_2O_4^{2-}$ anion breakdown. The present work was not, however, exclusively concerned with solid state reactivity because it has been shown that the breakdowns of some carboxylates proceed in a melt, e.g. [7]. In a previous comparable study [8] of the decomposition of calcium nitrate in the presence of several metal oxides, a principal conclusion was that melting was identified as a dominant control of reactivity. Metal cations, particularly those undergoing facile valence changes, were shown to be active in promoting nitrate anion breakdown. The present work extends previous investigations of oxalate anion breakdown to consider the possible roles of melting and of cation participation in mixtures of $K_2C_2O_4{\cdot}H_2O$ (POM) with ZnO, PbO, NiO, CuO, Cu_2O, Fe_2O_3, Co_3O_4 and Cr_2O_3, in oxidising (air) and reducing (hydrogen) flowing atmospheres.

2. Experimental

2.1. Materials

Potassium oxalate monohydrate ($K_2C_2O_4{\cdot}H_2O$), referred to here as POM, the parent material in the present study, was an analytical grade material, AnalaR product (England). It was carefully crushed in an agate mortar before use with no further treatment. Eight different metal oxides, ZnO, PbO, NiO, CuO, Cu_2O, Fe_2O_3, Co_3O_4 and Cr_2O_3 were prepared via direct calcination, for 3 h in air, of their corresponding analytical grade nitrates. Each metal nitrate was heated at the suitable temperature required to form the corresponding oxide. The metal oxides produced were characterised by X-ray diffraction to confirm that there had been complete decomposition of the nitrate to the oxide.

2.2. Preparation of 1:1 molar mixtures of POM: metal oxide

For each reactant mixture investigated, the calculated masses of POM and the required oxide were mixed thoroughly and were carefully crushed in an agate mortar for 1 h to ensure particle size homogeneity. Each reactant mixture was then stored in a sample bottle in a desiccator over $CaCl_2$.

2.3. Techniques

2.3.1. Thermal analysis

Thermal analysis measurements (thermogravimetry, TG, derivative thermogravimetry, DTG, and differential thermal analysis, DTA) were carried out by means of a Shimadzu "Stand-Alone" thermal analyser (TGA-50H and DTA-50), Japan. The thermal analyser included a data acquisition and handling system (TA-50WSI).

Thermal analysis experiments were performed in dynamic atmospheres (40 ml/min) of air or of hydrogen, at a heating rate of 10 °C/min. Experiments were usually carried out three times, under identical experimental conditions, and each reported mass loss is the average of three TG experiments for measurements that agreed to better than 1%. To remove the effects of variations of sample masses and particle sizes on the thermal analysis responses (e.g. peak shape and peak temperature) [9], equal masses (ca. 10–15 mg) of the crushed samples of reactant mixtures were always used. The TG instrument was re-calibrated at frequent intervals; the accuracy was always better than ±0.1 mg.

Highly sintered α-Al_2O_3 powder (Shimadzu) was used as the reference material in DTA experiments. Calibration of the DTA instrument for temperature measurement was carried out using indium and zinc metals: melting points were 156.6 and 419.6 °C [10], respectively.

2.3.2. X-ray diffraction

X-ray powder diffraction analysis of the parent materials, the prepared metal oxides and the decomposition products of the reactant mixtures in air and in H_2 at different temperatures were carried out using a model D5000 Siemens diffractometer (Germany), Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 30 mA back monochromator). An on-line data acquisition and handling system permitted an automatic JCPDS library search and match (Diffrac AT software, Siemens) for phase identification.

3. Results and discussion

3.1. Characterisation of the metal oxides by X-ray diffraction

The X-ray diffraction patterns of the calcination products of the eight metal nitrates have been identified as the pure oxides (ZnO, PbO, NiO, CuO, Cu_2O, Fe_2O_3, Co_3O_4 and Cr_2O_3), where they matched the ICDD data for each oxide as follows: ZnO (36–1451); PbO (38–1477); NiO (4–835); CuO (5–661); Cu_2O (35–1091); Fe_2O_3 (33–664); Co_3O_4 (43–1003) and Cr_2O_3 (38–1479).

3.2. The dehydration reaction

The present research was primarily directed towards characterising the anion breakdown reactions, but because the TG and DTA dehydration responses were available, a comparative survey of water elimination from the several oxide mixtures prepared was included. It was confirmed that the measured TG mass losses, below 147 °C, for all the reactant mixtures was in accordance with expectation for the constituent water in the $K_2C_2O_4{\cdot}H_2O$ of each reactant mixture. This agreement, both for reactions in air and in hydrogen, was within experimental error, ±1.8%. TG, DTG and DTA data for the dehydrations and decompositions of pure POM and its 1:1 molar mixtures with metal oxides in flowing air or hydrogen atmospheres are summarised in Tables 1 and 2, respectively.

The endothermic DTA peak maximum for dehydration in air, see Table 1, occurred at 107 °C for the hydrate alone and between 111 and 117 °C for the oxide-containing mixtures (the first values in the last column), except for Fe_2O_3, where the value was relatively lower at 91 °C, for no identified reason. The overall mean (±S.D.) for dehydrations in air was 111 ± 7.5 °C, most of the error resulting from the unexplained difference with iron oxide. The small scatter of values noted for the other preparations is attributed to textural differences that slightly varies the relative ease of water escape from within each reactant mass and to its thermal conductivity. Results for dehydrations in hydrogen, see Table 2, gave slightly lower dehydration temperatures, the mean value of the DTA peak maximum was 103 ± 4 °C, again the exception was the mixture containing iron oxide, 97 °C, but the deviation was relatively smaller. The more facile dehydration in hydrogen is readily explained by increased ease of diffusive water loss and heat transfer due to the presence of this low-density gas within the reactant mass of powder particles.

The very small variations of dehydration rates are in accordance with expectation for differences between closely similar, but not identical, reactant samples. All the evidence is consistent with the view that the rates of water loss from $K_2C_2O_4{\cdot}H_2O$ were constant for all the mixtures studied here, variations being within the degree of reproducibility expected.

3.3. The decomposition of potassium oxalate monohydrate (POM)

Fig. 1 shows TG and DTA curves for the decomposition of the potassium oxalate monohydrate (POM)

Table 1
Summary of the TG and DTA results obtained on heating pure potassium oxalate monohydrate (POM) and its 1:1 molar mixtures with different metal oxides at 10 °C/min in a dynamic atmosphere of air

Sample	Mass loss (%)		DTG peak maxima (°C)	T_i[a]	DTA peak maxima (°C)[b]
	Practical	Theoretical[c]			
Pure POM	24.90	24.98	122, 587	513	107 (n), 399 (n), 456 (n), 590 (x)
POM + ZnO	16.91	17.3	113, 588	515	112 (n), 399 (n), 450 (n), 593 (x)
POM + PbO	10.80	11.3	107, 588	460	111 (n), 399 (n), 470 (n), 590 (x)
POM + NiO	18.05	17.8	115, 585	329	117 (n), 398 (n), 482 (n), 587 (x)
POM + CuO	18.17	17.5	116, 465, 583	220	117 (n), 396 (n), 457 (n), 587 (x)
POM + Cu_2O	13.37	14.07	114, 510, 583	463	117 (n), 395 (n), 482 (n), 586 (x)
POM + Fe_2O_3	13.82	13.4	104, 382, 585	356	91 (n), 396 (n), 442 (n), 585 (x)
POM + Co_3O_4	10.78	10.83	113, 556	326	111 (n), 399 (n), 448 (n), 585 (x)
POM + Cr_2O_3	19.19	13.7	113, 469, 577	234	114 (n), 396 (n), 466 (n), 587 (x)

[a] The lowest temperature at which the cumulative mass change becomes detectable [17], (following dehydration).

[b] n (endo), x (exo).

[c] Theoretical mass loss at 630 °C assuming the formation of potassium carbonate together with the unchanged metal oxide.

at 10 °C/min in air and in H_2 atmospheres. The TG curve in air displays two mass loss steps, which are attributed to the dehydration (ca. 100–130 °C) and the decomposition (ca. 500–610 °C) processes. The mass loss values were 9.8 and 15.1%, respectively. These values are in agreement with expectation for the dehydration through loss of one mole of water ($-H_2O = 9.78\%$) and the subsequent decomposition of the anhydrous potassium oxalate to form potassium carbonate ($-CO = 15.2\%$). The average total mass loss at 650 °C (ca. $24.9 \pm 0.1\%$) agrees with theoretical expectation for the formation of K_2CO_3 (ca. 24.98%).

$$K_2C_2O_4 \rightarrow K_2CO_3 + CO \tag{1}$$

Fig. 1 also shows that the TG in H_2 is similar to that in air except that the decomposition step was relatively faster (decomposition temperature was 513 °C in air compared with 480 °C in H_2, see Tables 1 and 2).

The main features of the DTA trace for the reaction in air were the large dehydration endotherm (peak maximum 107 °C), a sharp endotherm at 399 °C

Table 2
Summary of the TG and DTA results obtained on heating pure potassium oxalate monohydrate (POM) and its 1:1 molar mixtures with different metal oxides at 10 °C/min in a dynamic atmosphere of hydrogen

Sample	Mass loss (%)		DTG peak maxima (°C)	T_i[a]	DTA peak maxima (°C)[b]
	Practical	Theoretical[c]			
Pure POM	25.07	24.98	111, 570	480	110 (n), 399 (n), 459 (n), 585 (n)
POM + ZnO	17.25	17.30	104, 570	517	104 (n), 280 (x), 399 (n), 456 (n), 589 (n)
POM + PbO	15.86	14.72	111, 463, 567	420	98 (n), 312 (x), 399 (n), 579 (n)
POM + NiO	24.31	24.23	112, 326, 587	300	104 (n), 294 (x), 398 (n), 499 (n), 592 (n)
POM + CuO	24.84	24.24	114, 244, 588	223	107 (n), 230 (x), 396 (n), 587 (n)
POM + Cu_2O	20.69	18.26	103, 258, 579	248	104 (n), 288 (x), 396 (n), 583 (n)
POM + Fe_2O_3	28.10	27.75	96, 392, 492, 589	362	97 (n), 272 (n), 346 (n), 396 (n), 446 (n), 589 (x)
POM + Co_3O_4	26.80	25.83	106, 399, 569	344	101 (n), 261 (x), 321 (x), 394 (x), 572 (x)
POM + Cr_2O_3	17.14	13.7	98, 461, 583	217	101 (n), 284 (x), 396 (n), 577 (n), 587 (n)

[a] The lowest temperature at which mass loss becomes appreciable [17], (following dehydration).

[b] n (endo), x (exo).

[c] Theoretical mass loss at 630 °C assuming the formation of potassium carbonate and the corresponding metal, except for the mixtures containing Cr_2O_3 and ZnO.

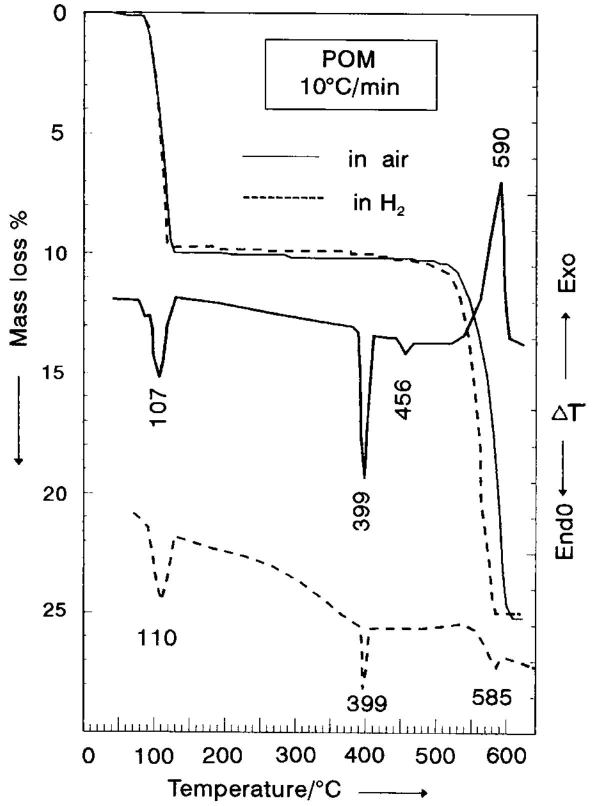

Fig. 1. TG and DTA curves for the decomposition of potassium oxalate monohydrate at 10 °C/min in a dynamic atmosphere of air (—) and in H_2 (- - -).

identified as melting and a large exotherm during decomposition (590 °C). There was one further, very small, endotherm at 456 °C, which was not characterised. The first two DTA peaks for POM decomposition in hydrogen were closely similar, but the decomposition exotherm was changed to a much smaller rise followed by a much smaller endotherm at 585 °C. This change may be a result of the elimination of the highly exothermic CO oxidation in air, when the hydrogen atmosphere was present.

3.4. The decompositions of mixtures of POM and oxides

Fig. 2a–h shows the TG curves for the decompositions, in air and in H_2, of all eight reactant mixtures, originally containing equimolar quantities of POM and ZnO, PbO, NiO, CuO, Cu_2O, Fe_2O_3, Co_3O_4 or Cr_2O_3, respectively. DTA curves for the decomposition of these eight reactant mixtures, in air and in H_2, are given in Fig. 3a–h and the response peak maxima are given in Tables 1 and 2. The data of Table 1 show that, with the exception of the Cr_2O_3 mixture, each mass loss, on completion of anion decomposition on heating in air to 630 °C, was in fair agreement with expectation from Eq. (1). In the hydrogen atmosphere, however, the overall mass losses, see Table 2, were greater and corresponded approximately with expectation for the same anion breakdown, together with oxide reduction to the metal in the mixtures containing PbO, NiO, CuO, Cu_2O, Fe_2O_3 and Co_3O_4.

The sharp DTA endotherm at 397 ± 2 °C (in both atmospheres) is identified as the melting of anhydrous potassium oxalate with no corresponding response, as expected, in the TG traces. This peak was present in all the mixtures studied, see Fig. 3a–h and Tables 1 and 2, and there was no perceptible broadening or other identifiable modification.

The characteristic features of the decomposition of each reactant mixture are discussed separately in the following sections.

3.4.1. Thermal reactions of ZnO + POM equimolar mixtures

Fig. 2a shows that all measured features identified on heating this reactant mixture were closely similar to those found for the reactions of pure POM. Above 500 °C, TG measurements showed a very slight increase in the rate of POM decomposition in hydrogen, but not in air across this temperature interval. The slight enhancing effect of H_2 is clear from the DTG peak (which gives the temperature corresponding to the maximum rate of mass loss) of the decomposition process, i.e. 588 °C in air compared with 570 °C in H_2, see Tables 1 and 2. The mass losses were, see Tables 1 and 2, consistent with dehydration at 112 °C and CO evolution, together with the formation of K_2CO_3, at 593 °C.

DTA responses in both atmospheres, Fig. 3a, included similarly positioned endotherms attributable to dehydration and the sharp response for melting at 399 °C. The decomposition in air, DTA peak maximum at 593 °C, was strongly exothermic and in hydrogen, there was a very minor modification of the response, compared with POM, which resulted in just detectable endothermic peak at 589 °C. X-ray

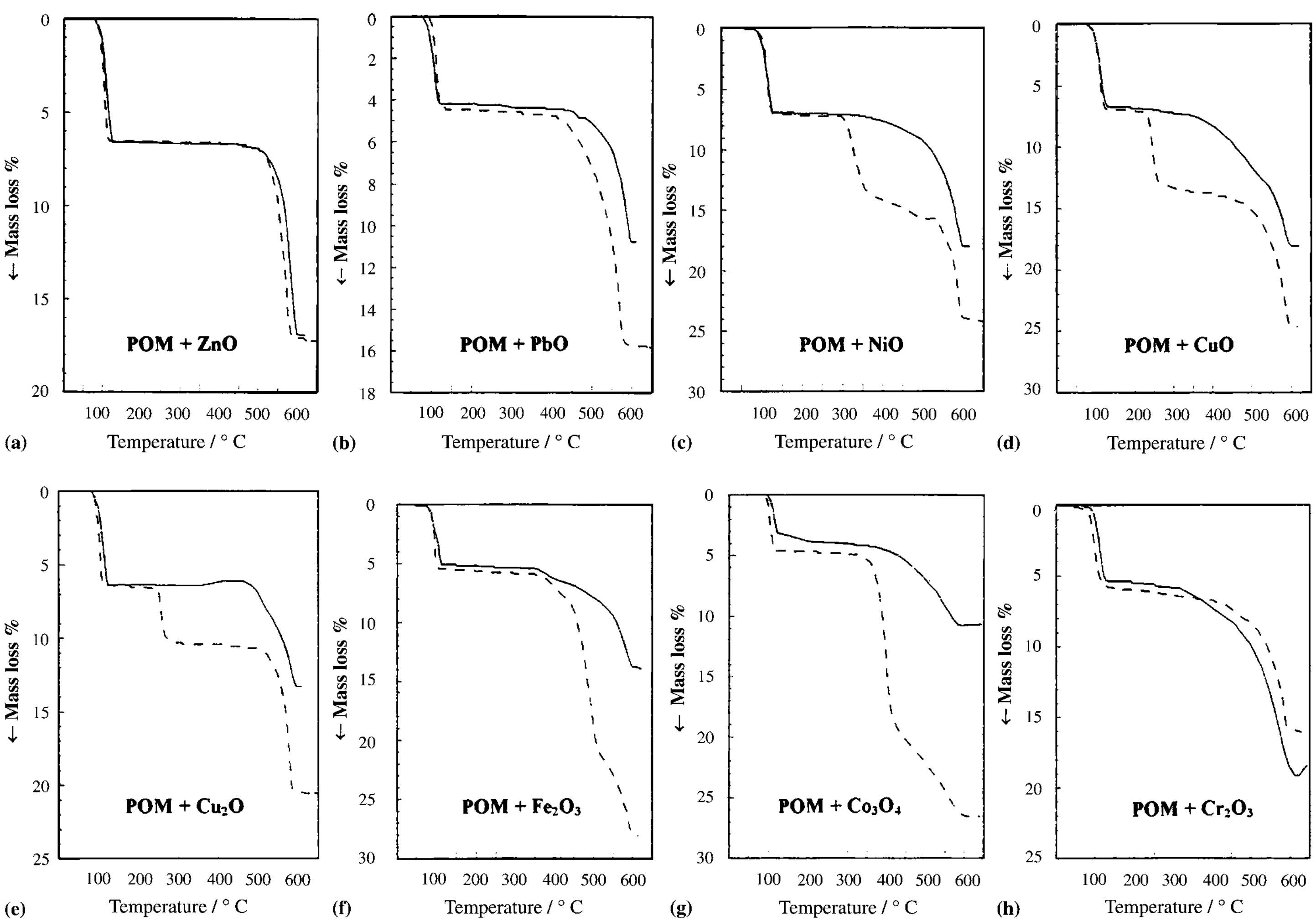

Fig. 2. TG curves of the decomposition of 1:1 molar mixtures of POM + metal oxide indicated at a heating rate of 10 °C/min in dynamic atmospheres of air (—) or of H_2 (- - -).

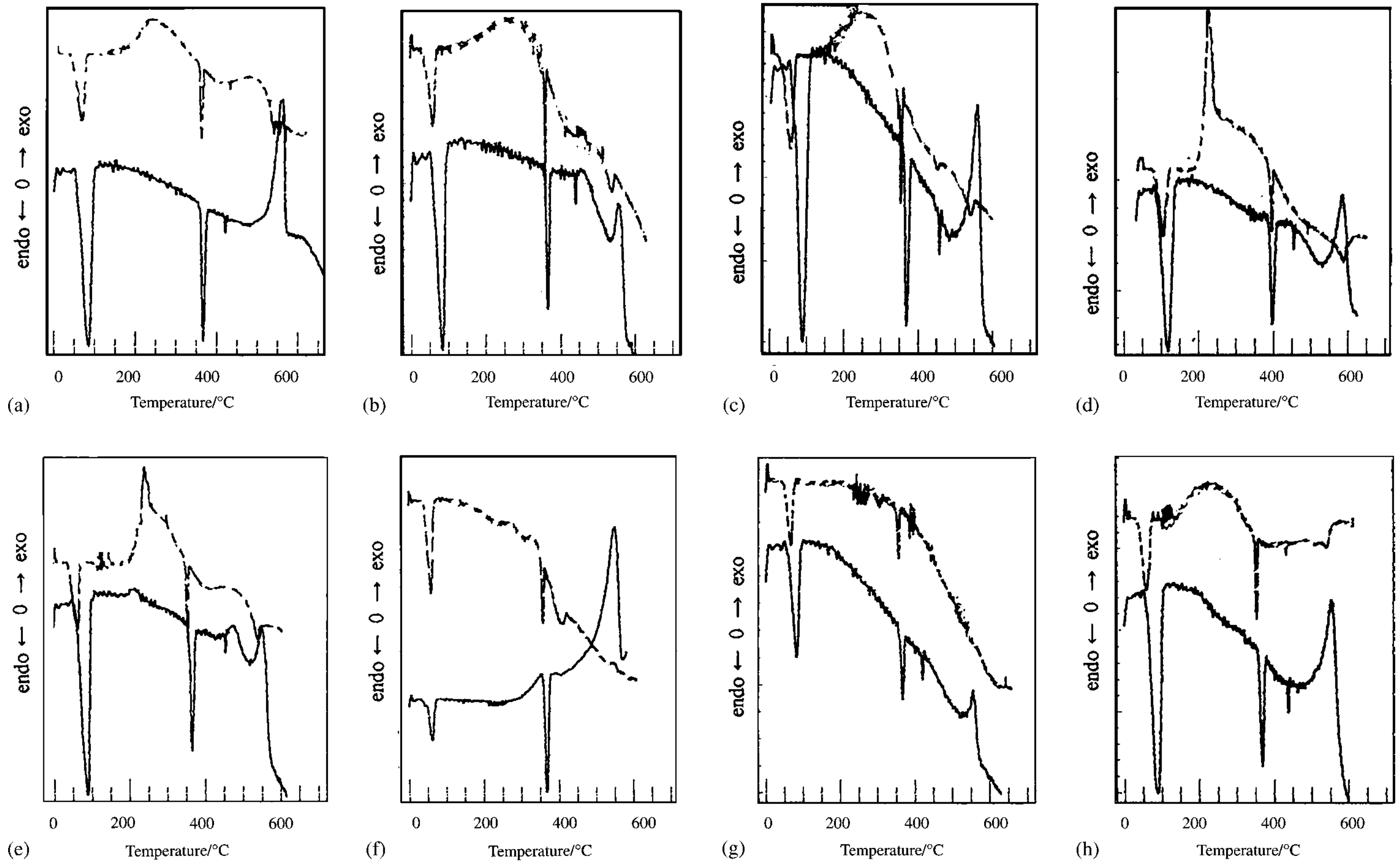

Fig. 3. DTA curves of the decomposition of 1:1 molar mixtures of POM + metal oxides at a heating rate of 10 °C/min in dynamic atmospheres of air (—) or of H_2 (- - -), where (a) POM + ZnO; (b) POM + PbO; (c) POM + NiO; (d) POM + CuO; (e) POM + Cu_2O; (f) POM + Fe_2O_3; (g) POM + Co_3O_4; and (h) POM + Cr_2O_3.

Table 3
Summary of XRD results for the decomposition products of pure potassium oxalate monohydrate (POM) and its 1:1 molar mixtures with different metal oxides after heating in air (at 630 °C) and in hydrogen (at different temperatures)

Sample	In air at 630 °C	In H_2 atmosphere at the temperatures indicated
Pure POM	K_2CO_3 (only)	At 630 °C K_2CO_3 (only)
POM + ZnO	ZnO (major), K_2CO_3 (major)	At 630 °C (ZnO (major), K_2CO_3 (major))
POM + PbO	PbO (major), K_2CO_3 (major)	At 630 °C (Pb (major), K_2CO_3 (major))
POM + NiO	NiO (major), K_2CO_3 (major)	At 400 °C (Ni (major), K_2CO_3 (major))
POM + CuO	CuO (major), K_2CO_3 (major)	At 300 °C (Cu (major), $K_2C_2O_4$ (major), K_3CuO_2 (minor))
POM + Cu_2O	CuO (major), K_2CO_3 (major)	At 300 °C (Cu (major), $K_2C_2O_4$ (major))
POM + Fe_2O_3	Fe_2O_3 (major), K_2CO_3 (major), K_2FeO_4 (minor), $K_2Fe_{22}O_{34}$(minor)	At 400 °C (Fe (major), K_2CO_3 (major), $KFeO_2$ (minor))
POM + Co_3O_4	Co_3O_4 (major), K_2CO_3 (minor), K_2CoO_3 (minor)	At 400 °C (Co_3O_4 (minor), Co (major), K_2CO_3 (minor), K_2CoO_3 (minor))
POM + Cr_2O_3	$K_2Cr_2O_7$ (major), K_2CO_3 (major), K_2CrO_4 (minor)	At 470 °C (Cr_2O_3 (major), K_2CO_3 (major), K_4CrO_4 (minor))

diffraction has shown, see Table 3, the formation of mixture of K_2CO_3 and ZnO on heating in air or in H_2. This is consistent with the mass loss measurements in both atmospheres. Zinc oxide exhibited no significant influence in promoting POM decomposition.

3.4.2. Thermal reactions of PbO + POM equimolar mixtures

Mass losses identified as oxalate decomposition became detectable at 460 °C in air and 420 °C in H_2, see Fig. 2b, which were significantly below values characteristic of POM (513 °C in air and 480 °C in H_2). The TG measurements detected the onset of oxalate breakdown above 460 °C in air, reaction occurring in the melt somewhat above the temperature at which lead oxalate decomposes in the solid state [11]. This reaction was slightly more rapid in hydrogen, where there is evidence that PbO is reduced to Pb and it is known [11] that lead metal catalyses PbC_2O_4 breakdown. The present observations show that the presence of lead, as Pb^{2+} or the metal, promotes POM decomposition. This may involve intervention of the relatively less stable lead oxalate, known to breakdown in this temperature interval. The overall mass loss on completion of decomposition in air (10.8%) was consistent with theoretical expectation (11.3%) for release of CO (Eq. (1)), but in hydrogen (15.86%) was significantly greater, ascribed to complete reduction of the oxide between 387 and 556 °C ($PbO + H_2 \rightarrow Pb + H_2O$). The overall mass loss in H_2 was in agreement with theoretical expectation for the reduction of PbO to Pb metal and the formation of K_2CO_3 (ca. 14.72%).

The two DTA endotherms, Fig. 3b, due to dehydration and the sharp melting response for POM, were not appreciably changed by the addition of the oxide, see Tables 1 and 2. The DTA exotherm for decomposition in air was markedly diminished for the mixture compared with the pure POM.

Table 3 shows the formation of PbO and K_2CO_3 as the solid decomposition products in air, while Pb metal together with K_2CO_3 were the products in H_2.

3.4.3. Thermal reactions of NiO + POM equimolar mixtures

Fig. 2c shows that on heating in air, a very slow reaction became detectable by TG above 329 °C, but only a small proportion (about 10%) of the oxalate anion had decomposed at the melting point of the anhydrous salt. About half of the oxalate had decomposed before the onset of the main DTA exothermic response of POM at 587 °C. In hydrogen, the mass loss between 287 and 357 °C is that expected for NiO reduction to the metal. The subsequent TG curve is similar to that for salt decomposition in the absence of the oxide between 527 and 593 °C.

The onset of slow decomposition was detected at temperatures significantly above that of nickel oxalate decomposition, 247 °C [11], and did not occur rapidly even in the melt well above this temperature. These results identify NiO as a catalyst of very low activity for oxalate breakdown and the activity of nickel metal is effectively zero.

DTA curves, Fig. 3c, shows the shift towards lower temperature of the dehydration endotherm in H_2 compared to its position in air. Both DTA curves are otherwise broadly similar to those of the pure POM reactant (Fig. 1).

X-ray diffraction, Table 3, showed that the solid products on heating to 630 °C in air to be a mixture of NiO and K_2CO_3. In H_2 atmosphere, however, the solid products on heating to 400 °C were identified as a mixture of Ni metal together with K_2CO_3. These results are in accordance with the mass loss measurements in air and in hydrogen, Tables 1 and 2.

3.4.4. Thermal reactions of CuO + POM equimolar mixtures

The TG curves in air and in H_2 (Fig. 2d) showed that the onset of oxalate decomposition in air was detected above 220 °C followed by slow rate increase with temperature. Some 25% remaining anion breakdown occurred at the temperature characteristic of the pure salt, 587 °C. Mass loss in air (18.17%) was close to expectation from Eq. (1) (17.5%). In hydrogen, the mass loss between 217 and 267 °C is in accordance with expectation for the reduction of oxide to copper metal, detected also as a DTA exothermic response at 230 °C, see Fig. 3d. Mass loss in H_2 (24.84%) was close to expectation for the reduction of CuO to Cu metal and evolution of CO (24.24%). The activity of the metal in promoting anion decomposition was substantially less than that of the oxide and decomposition in hydrogen was completed at the temperature characteristic of the pure salt. As with nickel, it is concluded that the oxide showed some slight activity for promoting oxalate breakdown. There was, however, no detectable increase in activity at the salt melting point and there was no significant interaction between the components of the mixture to form copper oxalate, which decomposes at 247 °C [12,13].

X-ray diffraction results, Table 3, showed that solid products after calcination at 630 °C in air were CuO and K_2CO_3, which is in agreement with mass loss in air, Table 1. On heating to 300 °C in H_2, Cu metal, anhydrous $K_2C_2O_4$ and some K_3CuO_2 were identified as the solid products.

3.4.5. Thermal reactions of Cu_2O + POM equimolar mixtures

TG measurements for the reaction in air (Fig. 2e) showed a small mass increase between 357 and 447 °C, attributable to oxidation of Cu_2O. This overlapped with a mass loss identified as oxalate decomposition above 447 °C, that was completed through onset of the (apparently uncatalysed) potassium oxalate breakdown reaction, detected by the characteristic DTA response at about 586 °C. X-ray diffraction of the calcination products at 630 °C showed, Table 3, the formation of CuO and K_2CO_3. In hydrogen there was a significant mass loss between 252 and 297 °C and an exothermic DTA peak maximum at 288 °C, see Fig. 3e, consistent with Cu_2O reduction to the metal. X-ray diffraction after heating to 300 °C in H_2 showed the production of Cu metal besides the undecomposed anhydrous $K_2C_2O_4$. The subsequent mass loss, and temperature of this reaction (above 512 °C), were in quantitative agreement with expectation for potassium oxalate decomposition which was not promoted below 587 °C by the metal Cu present.

The reaction in air confirms some slight ability of CuO to promote oxalate breakdown, but the metal and the lower oxide were effectively inactive. Previous studies [12,13] have shown that the decompositions of copper(II) carboxylates proceed in a somewhat lower temperature than the comparable copper(I) salts.

3.4.6. Thermal reactions of Fe_2O_3 + POM equimolar mixtures

Fig. 2f shows that in air, oxalate decomposition commenced close to the temperature of salt fusion, above 356 °C, and continued slowly during heating to 513 °C resulting in breakdown of about half of the $C_2O_4{}^{2-}$ content. The remainder decomposed in the temperature range close to that for the reaction of pure potassium oxalate. The DTA curve in air, Fig. 3f, had the same characteristics as that of the pure POM. The reaction in hydrogen showed that the initial reaction, above 356 °C, was about twice as rapid as in air, but this overlapped with oxide reduction between 447 and 507 °C. This conversion to metal apparently eliminated the low level of activity of the oxide and again about half of the potassium oxalate underwent apparently unpromoted decomposition only above 507 °C. The DTA curve in H_2 was rather similar to that in air with a very weak decomposition exothermic peak at 589 °C, see Fig. 3f.

The decomposition of iron(III) oxalate proceeds [6] rapidly below (137 °C) and iron(II) oxalate reacts above about 327 °C. The present observations show that Fe_2O_3 possesses some activity for promoting oxalate breakdown, but reaction proceeds to only a limited extent, perhaps due to some cation reduction. In a reducing atmosphere, the activity was further diminished by reduction of the iron ions to the metal.

X-ray diffraction of the calcination products at 630 °C characterised the solid products as Fe_2O_3, K_2CO_3 with smaller amounts of K_2FeO_4 and $K_2Fe_{22}O_{34}$. At 470 °C in H_2, however, Fe metal and K_2CO_3 were the major solid products with traces of $KFeO_2$. K_2FeO_4 and $K_2Fe_{22}O_{34}$ have been reported [14] to be formed during the decomposition of potassium ferrioxalate, $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. Potassium ferrioxalate was reported [14] to decompose in air between 260 and 315 °C to form $K_2C_2O_4$ and Fe_2O_3. Afterwards, potassium oxalate decomposes to produce K_2CO_3 between 315 and 360 °C, i.e. at much lower temperature than its decomposition in the present study (ca. 513 °C). Similarly, the decomposition of this complex in H_2 (or N_2) atmosphere produces $K_2C_2O_4$ (between 300 and 345 °C) which decomposes to K_2CO_3 at 345–407 °C.

3.4.7. Thermal reactions of Co_3O_4 + POM equimolar mixtures

Fig. 2g shows that oxalate breakdown in air became detectable at 326 °C and the rate increased slowly with temperature almost reaching completion at 590 °C. A very small DTA response was detected, see Fig. 3g, at the temperature of potassium oxalate breakdown, 585 °C. X-ray analysis, Table 3, showed that on heating to 630 °C in air, the solid decomposition products were Co_3O_4 with relatively smaller amounts of K_2CO_3 and potassium cobalt oxide (K_2CoO_3). In hydrogen, oxide reduction proceeded between 327 and 427 °C. Decomposition of oxalate was completed, at a rate comparable with that of the reaction in air in the interval 427–577 °C. The decomposition products in H_2 at 400 °C were cobalt metal, Co_3O_4, K_2CO_3 and K_2CoO_3.

Cobalt oxide was identified as relatively the most active of the oxides studied here for promoting breakdown of the oxalate ion in the potassium salt, but the levels of such activity were very low. These mixtures also contained the highest proportion of added oxide.

3.4.8. Thermal reactions of Cr_2O_3 + POM equimolar mixtures

Fig. 2h displays the TG curves of the decomposition of this mixture in air and in H_2. The mass loss from this reactant mixture in air (Table 1) was, unlike all the others investigated, appreciably greater than expectation, possibly due to some oxidation to potassium chromate with consequent release of CO_2. X-ray analysis results of the decomposition products on heating to 630 °C in air were identified to be potassium dichromate $K_2Cr_2O_7$ and K_2CO_3 as major constituents together with potassium chromate K_2CrO_4 as a minor phase. The total mass loss was relatively less for reactions in hydrogen, but was nevertheless significant. After heating to 470 °C in H_2, the decomposition products were Cr_2O_3 and K_2CO_3 together with potassium chromium oxide, K_4CrO_4, as a minor phase. In air, the onset of mass loss attributable to oxalate ion breakdown became detectable at 234 °C and the rate slowly increased with temperature, but was completed only above 587 °C with about 25% breakdown of potassium oxalate. The reaction in hydrogen was closely similar: as anticipated, there was no evidence of oxide reduction to the metal. DTA curves of this mixture in both atmospheres are given in Fig. 3h.

4. Conclusions

The principal result from this research programme was not anticipated: all of the several oxides investigated exhibited very low abilities to promote the breakdown of molten potassium oxalate. The work was originally undertaken to determine whether the anion decomposition proceeded either through a heterogeneous catalytic decomposition reaction on the surface of the various added oxides, the metal formed by reduction or involved the intervention of the metal oxalate, or both. The decompositions of all oxalates envisaged as possibly participating as intermediates are known [1] to react in the solid state 150 °C or more below the temperature of decomposition of potassium oxalate (above 500 °C). It was also thought that reactions might proceed more rapidly in the melt [15]; $K_2C_2O_4$ melts at 399 °C, but no changes in reactivity could be identified as being associated with this temperature. This contrasts with the behaviour found [8] for calcium nitrate in mixtures which also contained several of the oxides studied here. The present results showed that in the presence of these transition metal oxides the rates of oxalate breakdown were very slow. The amounts that reacted before onset of molten POM decomposition did not increase significantly with temperature. In every mixture studied, even when oxide-promoted reaction was detected, a proportion of POM breakdown occurred at the temperature characteristic of the uncatalysed reaction, often half or more of the reaction proceeding in this stage. All the oxides studied showed very low catalytic activity for the promotion of this reaction: evidently the formation of dissolved transition metal oxalate, or alternatively the solid oxalate, did not offer a different and effective degradation mechanism.

We conclude that within the ionic molten salt, potassium oxalate ($2K^+ + C_2O_4^{2-}$), the metal cations of the oxides studied were either insoluble or did not form the covalent $^+M\text{-}OCO_3{}^-$ linkages that participate in solid state decompositions (or both). It is well-known [16] that the ionic perchlorates (and related compounds) are more stable than their covalent counterparts. Here, the formation of divalent or trivalent oxalates apparently cannot proceed so that this route to anion breakdown is effectively unavailable. The approximate temperatures of solid metal oxalate decompositions are, from [6,11–13] and references cited therein: ZnC_2O_4 347 °C, PbC_2O_4 347 °C, NiC_2O_4 247 °C, CuC_2O_4 ($Cu_2C_2O_4$) 247 °C, $Fe_2(C_2O_4)_3$ 137 °C, FeC_2O_4 327 °C, CoC_2O_4 307 °C and $Cr_2(C_2O_4)_3$ about 427 °C. The melting point of $K_2C_2O_4$ was 399 °C, and unchanged (DTA) by the presence of oxides in all these mixtures, decomposition commenced, TG, at 513 °C with the DTA peak maximum at 590 °C and was completed by 627 °C.

Two criteria may be used to sequence the relative abilities of these low activity catalysts in promoting breakdown of the oxalate ion. One such criterion is the extent of reaction prior to the unpromoted breakdown of $K_2C_2O_4$: this, easily recognised, reaction was initiated at 513 °C (TG), the DTA peak maximum at 590 °C with completion by 627 °C. For all the present reaction mixtures, heated at 10 °C/min in a dynamic atmosphere of air or hydrogen, this characteristic response was detected, showing that the promoted decompositions, even in the presence of relatively large amounts of these possible catalysts, did not result in the completed breakdown of POM in the original reactant. The amounts of this reaction that were estimated (DTA) to have occurred below about 547 °C in air diminished for the following sequence of added oxides:

$$Co_3O_4 > Fe_2O_3,\ NiO > PbO > CuO,$$
$$Cu_2O > Cr_2O_3 > ZnO$$

In hydrogen, the relative activities of those oxides capable of reduction were significantly diminished. The alternative criterion for comparing reactivities was the temperature of onset of detectable (TG) reaction, these increased in the following sequence with air:

$$CuO < Cr_2O_3 < Co_3O_4,$$
$$NiO < Fe_2O_3 < PbO < Cu_2O < ZnO$$

Again, the ability of hydrogen to reduce the oxide to metal diminished the already low levels of reactivity. Neither of these sequences of correlations agreed particularly satisfactorily with the stabilities of the corresponding metallic oxalates, which increase in the approximate sequence:

$$Fe_2(C_2O_4)_3 < NiC_2O_4,$$
$$CuC_2O_4 < CoC_2O_4 < FeC_2O_4 < ZnC_2O_4,$$
$$PbC_2O_4 < Cr_2(C_2O_4)_3$$

Clearly, if oxalate intervention was an effective reaction pathway for oxalate breakdown, reactions of all the mixtures studied here would be completed well below the characteristic temperature of the potassium oxalate reaction, 507–627 °C. This was not observed. We also note that these low levels of activity were diminished even further for reactions taking place in hydrogen. The significant feature of this pattern of behaviour is that the initial slow reaction rates in these mixtures did not subsequently increase to give a pronounced DTA peak. The slow rates were maintained across relatively very wide temperature intervals without the expected (Arrhenius-type) increase. We interpret this as continued deactivation of the active participants, either by direct reduction of the oxide surface (e.g. by CO product, Eq. (1)) or through deposition here of product K_2CO_3 (Eq. (1)). This product (K_2CO_3) melts at a temperature above and outside the present range, 898 °C, and may not be readily soluble in the molten oxalate. Thus, all the presently investigated oxides, including those that might have been expected to form potassium salts (ZnO, PbO and Cr_2O_3), were unexpectedly inactive in promoting breakdown of the oxalate anion in the molten potassium salt. Because these transition metals, and some of their salts, are normally active in promoting carboxylate breakdown [1], there must be some effect preventing this apparently available reaction mechanism. Two possibilities are the inability of oxides to interact with the ionic species that constitute the molten potassium oxalate salt and/or there is poisoning (deactivation, blocking) of the oxide surface that inhibits or eliminates the possible participation of a heterogeneous catalytic reaction.

We conclude that the amounts of metal cations, from the oxides, that interact with POM to form oxalates is small. This is not an effective path for anion breakdown. Similarly, the surfaces of the oxides, or of the metals formed by their reduction, did not strongly promote oxalate decomposition by a heterogeneous catalytic-type reaction that may be the active surface in autocatalytic (nucleation and growth [1]) processes perhaps participating in some crystolysis reactions, such as the solid state decomposition of nickel oxalate.

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