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Thermogravimetric studies of the catalytic activity of molten alkali metal sulphate solutions of vanadium and niobium

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Abstract

The thermogravimetric analysis of potassium disulphate in the ternary sulphate eutectic (Li_2SO_4–Na_2SO_4–K_2SO_4) under various gas atmospheres (N_2, SO_2–N_2, SO_2–N_2–air) is described. Similar studies on solutions that also contain vanadium or vanadium and niobium, indicated the complex interaction of niobium in the vanadium oxidation–reduction processes and clarified the behaviour of promotors in the catalytic process.

INTRODUCTION

Molten sulphate catalyst is used for the catalytic oxidation of sulphur dioxide to sulphur trioxide which is a stage in the production of sulphuric acid, the inorganic chemical produced in highest tonnage on a world-wide basis. Hence, this catalyst system should be considered as one of the most important uses of molten salts. Therefore, it is surprising that the catalytic reactions involved are still not completely understood.

This is due in part to the complexity of the system; the melt initially consists of alkali metal sulphates with vanadium(V) oxide (or its thermal precursor, NH_4VO_3) to which may be added one or more of a whole variety of "promotors", mostly other transition metals but also including some "p-block" compounds. However, in contact with the gas phase (air + SO_2) at temperatures in the range 420–580 ° C, a series of di- and higher sulphates are formed with at least two or, possibly, three oxidation states of vanadium and also, possibly, of the promotor; these frequently interact to form polymeric species at the concentrations employed. Many species have been postulated but recent studies have suggested that the following are present in disulphate–sulphate melts: $KVO(SO_4)_2$ [1,2], KVO_2SO_4 [1], $K_3VO_2(SO_4)S_2O_7$ [1,2], $K_4(VO_2)_2(SO_4)_2S_2O_7$ and $K_3VO_2(SO_4)_2$ [3]. Because the catalyst melts are normally supported on kieselguhr there is the further possibility of reactions involving silica, and also of other solid–liquid interactions. Some of the latter are certainly important as a vanadium(IV) compound ($K_4(VO)_3(SO_4)_5$) has been shown to crystallise from such melts

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[4], and a vanadium(III) compound ($KV(SO_4)_2$) has been shown to crystallise from similar melts containing hydrogen sulphate [5].

Fundamental studies have usually involved simplification of the actual catalyst system, for example to avoid the complications of low solubilities and high viscosities at the lower end of the temperature range. Among those used are melts containing $KHSO_4$ [5], or melts based on the ternary alkali metal sulphate eutectic [6]. The latter approach, used here, also allows comparison to be made with the considerable amount of systematic chemistry now known for the ternary sulphate eutectic.

Such fundamental studies have used mostly catalytic, potentiometric and spectroscopic methods, but little use has so far been made of thermogravimetric techniques. This paper describes how such measurements, together with quantitative analysis, can readily provide further information on the interactions between the different parameters.

EXPERIMENTAL

Materials

The ternary eutectic (78 mol.% Li_2SO_4, 8.5 mol.% Na_2SO_4 and 13.5 mol.% K_2SO_4, m.p. 512°C) was prepared as previously described [7]. Vanadium(V) oxide and niobium(V) oxide (reagent grades) were dried for 4 hours at 200°C. Potassium disulphate was prepared by heating potassium persulphate (AnalaR) for 5 hours at 220°C [7].

The gas atmosphere was mixed from cylinder gases, sulphur dioxide (BOC 99.8%) and air (BOC compressed air) passed through concentrated sulphuric acid, potassium hydroxide solution and then silica gel, and nitrogen (BOC oxygen-free), passed through a chromium(II) bubbler before being dried in the same way. The proportions of the dried gases and the flow rates (400–600 ml min^{-1}) were controlled with GAP flow meters and needle valves.

Procedure

Thermogravimetric analyses were carried out with a Stanton TR-1 thermobalance using a 10 ml gold crucible, either at a heating rate of 2°C min^{-1} or else isothermally. The balance was adapted for corrosive gases such that all evolved gas was drawn out of the top of the furnace with a pump. To avoid surface effects, the silica support rod was renewed every 10 runs and the silica sheath every 20 runs.

The gas leaving the balance was drawn through two traps containing a propan-2-ol/water mixture (4:1 by volume) and then through a sintered glass filter (No. 4 porosity) before being discharged into a fume cupboard. All ground-glass surfaces were lubricated with syrupy phosphoric acid.

Analysis

The crucible was quickly removed from the support rod at the end of an experiment, and then nitrogen was flushed through the balance until no white mist of sulphur trioxide was visible. The propan-2-ol/water mixture, together with washings of the filter, etc., were boiled to half-volume to remove dissolved sulphur dioxide. Excess 0.1 M barium perchlorate was added to precipitate barium sulphate and the excess was titrated with 0.1 M sodium sulphate (pH 2–3) using nitrosulphanaza III as indicator [8].

The quenched melt in the crucible was dissolved in 2 M sulphuric acid and the vanadium(IV) was titrated against permanganate. Total vanadium could then be estimated as vanadium(IV) after reduction with sulphur dioxide and boiling to half-volume to remove excess gas.

Experiments were repeated 2–3 times, and where the weight increased or decreased, or when the vanadium(IV) percentage varied by more than one standard deviation (2–4%) of the mean, the experiments were discarded.

A Philips X-ray powder diffractometer using copper $K\alpha$ radiation was used to identify the solid samples. The *d*-spacings and intensities of the lines obtained (full lists in ref. 9) were matched with those in the JCPDS Index.

RESULTS

The decomposition of potassium disulphate in the ternary sulphate eutectic was relatively insensitive to the gaseous atmosphere (Fig. 1, curves A, B and C), but occurred at significantly lower temperatures than for the disulphate heated without eutectic (Fig. 1, curve D), a result attributed to the polarising effect of the lithium cations [6].

When mixtures of potassium disulphate and vanadium(V) oxide were heated under a sulphur dioxide–nitrogen atmosphere (10–90%), thermogravimetric curves of a characteristic shape were obtained (Fig. 2). The lowest temperature portion (to approximately 430 ° C) showed a weight gain during which vanadium(IV) was formed. (Acidic aqueous solutions of the quenched reacted melt were blue, absorption maximum 13000 cm^{-1}, and were estimated with permanganate.) Above the temperature of the maximum of the weight gain, it was observed that the mixture was completely soluble in the eutectic and also that sulphur trioxide began to evolve, resulting eventually in an overall weight loss from the thermogravimetric crucible.

The initial weight gain was very nearly one millimole of sulphur dioxide for each millimole of vanadium(IV) formed and accorded with the equation

$$V_2O_5 + SO_2 + S_2O_7^{2-} \rightarrow 2VOSO_4 + SO_4^{2-} \qquad (1)$$

See, for example, expt. 10 in Table 1A.

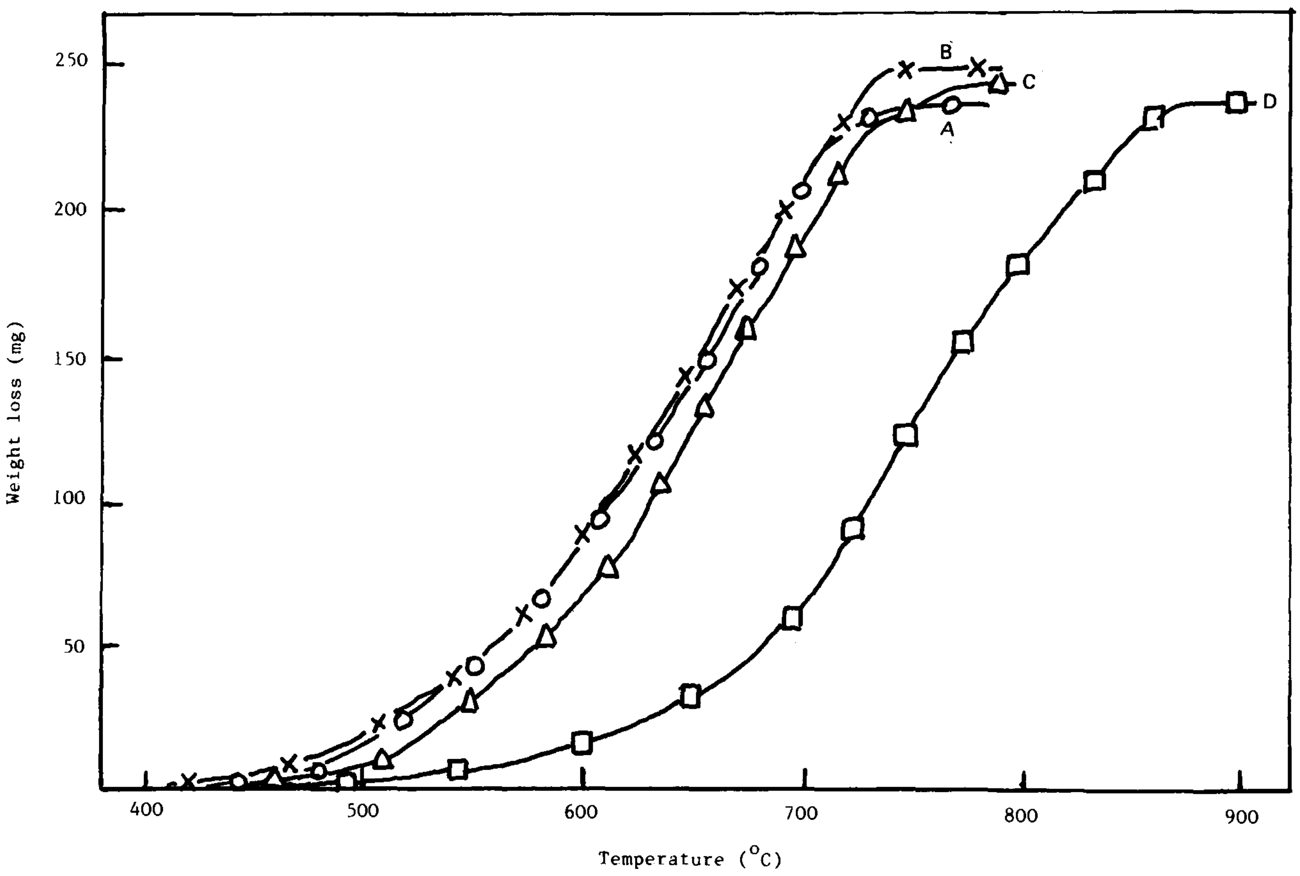

Fig. 1. Thermogravimetric analysis of potassium sulphate in ternary sulphate eutectic (3 g): curve A, ○, 3.02 mmol. $K_2S_2O_7$ under SO_2(10%)–N_2(90%); curve B, X, 3.20 mmol. $K_2S_2O_7$ under SO_2(10%)–N_2(30%)–air(60%); curve C, Δ, 3.17 mmol. $K_2S_2O_7$ under N_2; curve D, □, 3.00 mmol. $K_2S_2O_7$ under SO_2(10%)–N_2(90%).

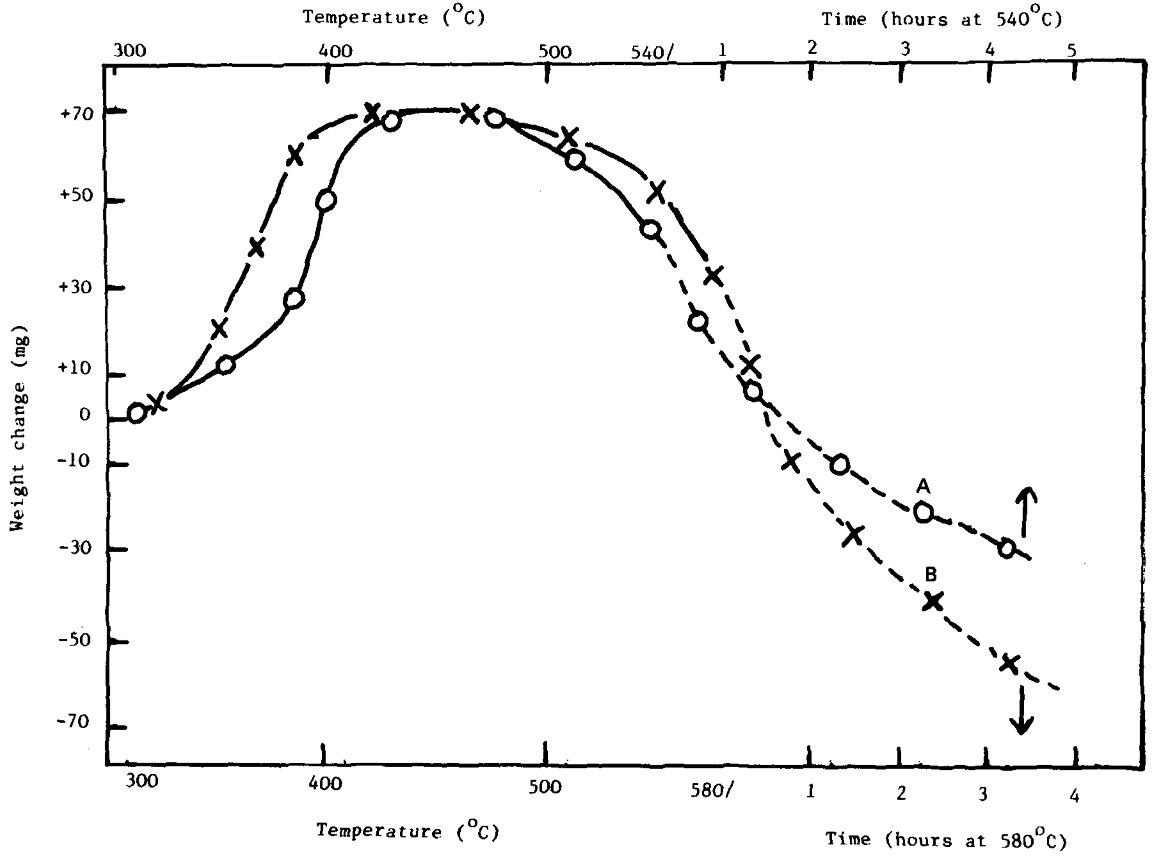

Fig. 2. Thermogravimetric analysis of vanadium(V) oxide (1.35 mmol.) with potassium disulphate (3.25 mmol.) in ternary sulphate eutectic (3 g) under SO_2(10%)–N_2(90%): curve A, ○ heated to 540 °C for 230 min (Expt. 9); curve B, ×, heated to 580 °C for 230 min (Expt. 12).

TABLE 1

Solutions in ternary sulphate eutectic (3 g) heated under SO_2(10%)–N_2(90%) in gold crucibles

Expt. no.	Wt. gain (mg) and temp. (°C)	Wt. loss to max. temp. (°C)	Wt. loss at max. temp. in time (m)	Total wt. loss (mg)	% V(IV) from $KMnO_4$ titn.	% V(IV) calc. from wt. gain	Calc. wt. gain from % V(IV)	Wt. of SO_3 in trap (mg)	Actual wt. change (mg)	Calc. wt. change (mg)
A. V_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (3.25 mmol.)										
10	67(300–430)	to maximum weight gain			80.0	77.5	69	4	+67	+65
11	67(300–430)	39(580)	90(230)	129	82.0	77.5	71	135	−62	−64
12	70(300–430)	43(580)	90(230)	133	79.0	81.0	68	135	−63	−65
8	69(300–430)	21(540)	67(270)	88	86.8	80.0	76	87	−19	−11
9	70(300–430)	21(540)	82(270)	103	86.8	81.0	76	99	−33	−23
B. V_2O_5 (1.35 mmol.) + Nb_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (6.5 mmol.)										
14	79(300–430)	to maximum weight gain			91.6	91.4	79	0	+79	+79
13	75(300–420)	20(580)	86(230)	106	76.0	86.8	66	103	−31	−32
15	72(300–430)	13(580)	76(230)	89	76.0	83.3	66	85	−17	−19
18	73(300–430)	15(580)	62(230)	77	78.3	84.5	68	72	−4	−4

The second weight-loss portion of the thermogravimetric curve (Fig. 2) was largely due to the loss of sulphur trioxide from the disulphate

$$S_2O_7^{2-} \rightarrow SO_4^{2-} + SO_3 \qquad (2)$$

as the weight of trapped sulphur trioxide was close to the weight loss which occurred with rising temperature and then isothermally (compare columns 5 and 9 of Table 1); it was also apparently independent of the extent of initial absorption of sulphur dioxide, as indicated by the similarity between the calculated (i.e. the difference between the weight gain of SO_2 calculated from the experimental V(IV) and the weight of SO_3 in the trap) and the actual overall weight change (columns 11 and 12 of Table 1A). The extent of the weight loss suggests that sulphur trioxide was more easily lost from a melt solution containing vanadium(IV) as well as vanadium(V) than from one containing only vanadium(V) (compare Fig. 4, curve B of ref. 6).

The observed equivalence between the vanadium(IV) remaining at the end of an experiment after heating to 580 °C (e.g. in experiments 11 and 12 of Table 1A) and the weight of sulphur dioxide absorbed during the first part of the thermogravimetric run, i.e. as if eqn. (1) is applicable only during this first part, is, however, fortuitous. This is shown in those experiments heated to a rather lower temperature (e.g. 540 °C, experiments 8 and 9 of Table 1A), because in these the vanadium(IV) concentration was rather higher even though the initial sulphur dioxide absorption was similar, and indicated that more sulphur dioxide had been absorbed above the temperature of the maximum weight gain (430 °C) with resulting formation of vanadium(IV). Heating to 580 °C, then, caused decomposition of some vanadium(IV) with formation of sulphur trioxide [10]. When air was added to the gas mixture (10% SO_2, 30% N_2, 60% air) the overall shape of the thermogravimetric curve remained the same (Fig. 3) but with quantitative changes (Table 2), the most notable being the increased weight of sulphur trioxide trapped despite the overall weight losses being similar to those without air. This indicated that catalytic oxidation of sulphur dioxide had occurred.

Once again, the two parts of the thermogravimetric curves were very largely independent of each other, as very little sulphur trioxide was released much below the temperature of the maximum weight gain (see in particular experiments 50, 51 and 52 of Table 2), as was also found with no air in the gas mixture (see experiment 10 of Table 1A). However, the initial process of reduction to vanadium(IV) appears to follow a slightly different stoichiometry when air is present, analogous to that suggested by Gushchina et al. [11]

$$V_2O_5 + 2SO_2 + \tfrac{1}{2}O_2 \rightarrow 2VOSO_4 \qquad (3)$$

in which oxygen was shown to be involved in the reduction. In our case, only 12% of the sulphur dioxide seems to have been oxidised, the equation

$$7V_2O_5 + 8SO_2 + \tfrac{1}{2}O_2 + 6S_2O_7^{2-} \rightarrow 14VOSO_4 + 6SO_4^{2-} \qquad (4)$$

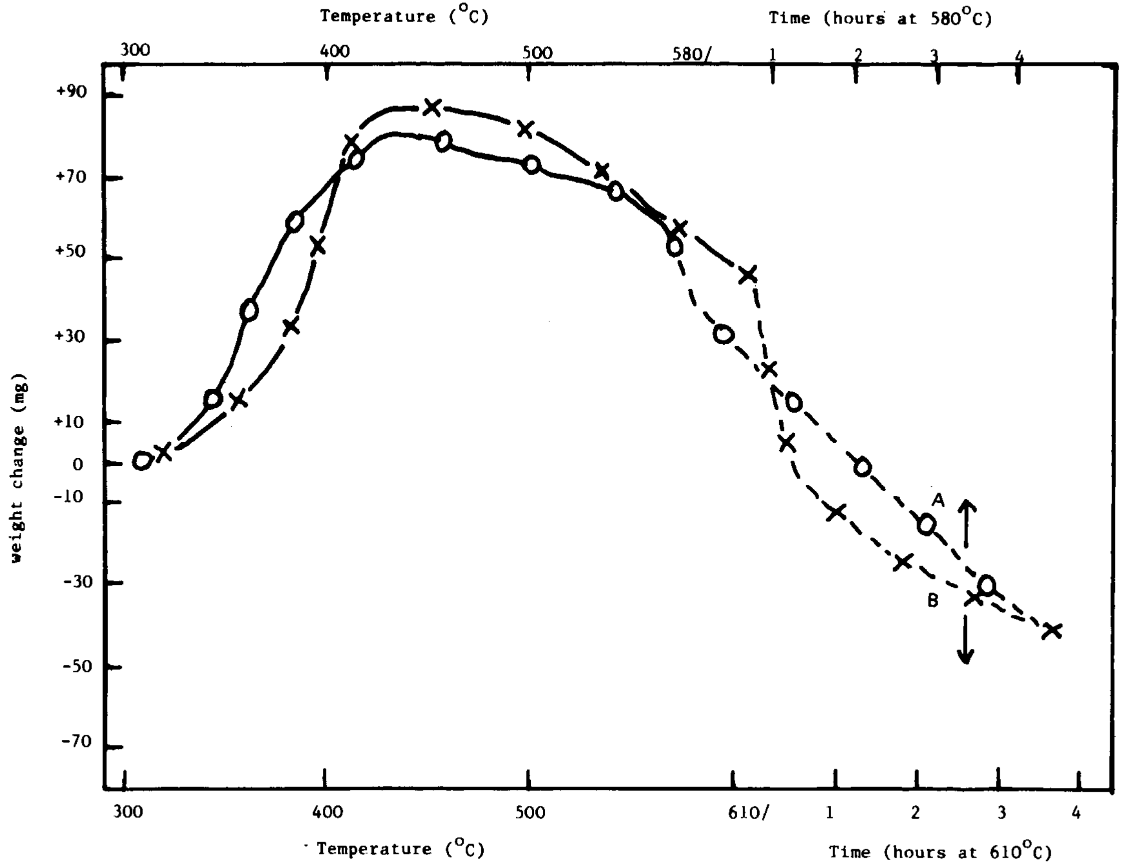

Fig. 3. Thermogravimetric analysis of vanadium(V) oxide (1.35 mmol.) with potassium disulphate (3.25 mmol.) in ternary sulphate eutectic (3 g) under SO_2(10%)–N_2(30%)–air(60%): curve A, o, heated to 580 °C for 230 min (Expt. 31); curve B, ×, heated to 610 °C for 230 min (Expt. 41).

TABLE 2

V_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (3.25 mmol.) in ternary sulphate eutectic (3 g) heated under SO_2(10%)–N_2(30%)–air(60%)

Expt. no.	Wt. gain (mg) and temp. (°C)	Wt. loss to max. temp. (°C)	Wt. loss at max. temp. in time (m)	Total wt. loss	% V(IV) from $KMnO_4$ titn.	Calc. wt. gain from % V(IV)	Wt. of SO_3 in trap (mg)	Actual wt. change (mg)	Calc. wt. change (mg)
33	83(300–440)	to maximum weight gain			83.9	83.5	2	+83	+81.5
31	82(310–430)	40(580)	77(230)	117	86.0	85.6	179	−35	−93
32	83(300–440)	40(580)	81(230)	121	80.0	82.6	172	−38	−86
41	87(300–440)	42(610)	88(230)	130	77.7	86.6	190	−43	−103
50	95(320–450)	−(450)	28(230)	28	91.5	94.5	33	+61	+62
51	90(320–450)	−(450)	30(230)	30	91.4	89.5	36	+60	+53.5
52	86(310–440)	−(450)	25(230)	25	85.0	86.6	23	+61	+64

which was derived by fitting the results of experiment 33, gave a reasonable correlation with the actual vanadium(IV) values found for the other experiments (compare columns 6 and 7 of Table 2). That oxidation of sulphur dioxide to sulphur trioxide largely took place at temperatures above the temperature of maximum weight gain can be well seen from Table 2, where for experiments held at these temperatures (Nos. 50, 51 and 52), the ratios of the weight of trapped sulphur trioxide to the total weight loss were much less than for experiments taken to 580 ° C (Nos. 31 and 32); but at 610 ° C (experiment 41), the ratio altered little.

When niobium(V) oxide was also added to the melt, the amount of potassium disulphate was doubled (thus keeping the transition metal : disulphate ratio constant): it was known that otherwise the greater ratio of transition metals would have stabilised the disulphate excessively [12]. The thermogravimetric curves obtained without air in the gas mixture (e.g. Fig. 4) showed the same features as before, though again with quantitative differences (Table 1B).

The first part of the reaction up to the temperature of maximum weight loss (experiment 14) was still well described by eqn. (1), although more vanadium(IV) was formed. At higher temperatures, there was less vanadium(IV) than expected from the size of the initial weight gain, suggesting that decomposition of vanadium(IV) was easier, perhaps because of stabilisation due to formation of a vanadium(V)–niobium(V)–disulphate polymer (vanadium(V) and niobium(V) have similar ionic radii). It was noted that less sulphur trioxide was evolved above 430 ° C when niobium(V) oxide was present (compare experiments 15 and 18 with 11 and 12, Table 1), though eqns. (1) and (2) still well expressed the overall weight loss, (compare columns 10 and 11).

Once more, when air was added to the gas mixture passing over the melt containing both vanadium and niobium, more sulphur trioxide was trapped than was indicated by the weight loss (Table 3) but these values were smaller than without niobium. However, the vanadium(IV) formed agreed quite well with the initial weight gain using eqn. (4), which in turn indicated that formation of the equilibrium concentration of vanadium(IV) was largely a lower temperature process, as was shown when the temperature was not taken higher than the temperature of maximum weight gain (Table 3B). In addition, the weight loss (Table 3B) was clearly less than when niobium was not present (Table 2), even though the amount of sulphur trioxide trapped was comparable, thus indicating that catalysis was possibly greater when niobium was present, a conclusion further supported by the lower temperature of the maximum weight gain (which may be an indicator of a lower bite catalyst).

When the proportion of sulphur dioxide in the gas mixture was reduced to 6% (Table 4), the weight gains and losses, and the trapped sulphur trioxide and vanadium(IV) found, were all very similar to those obtained with the

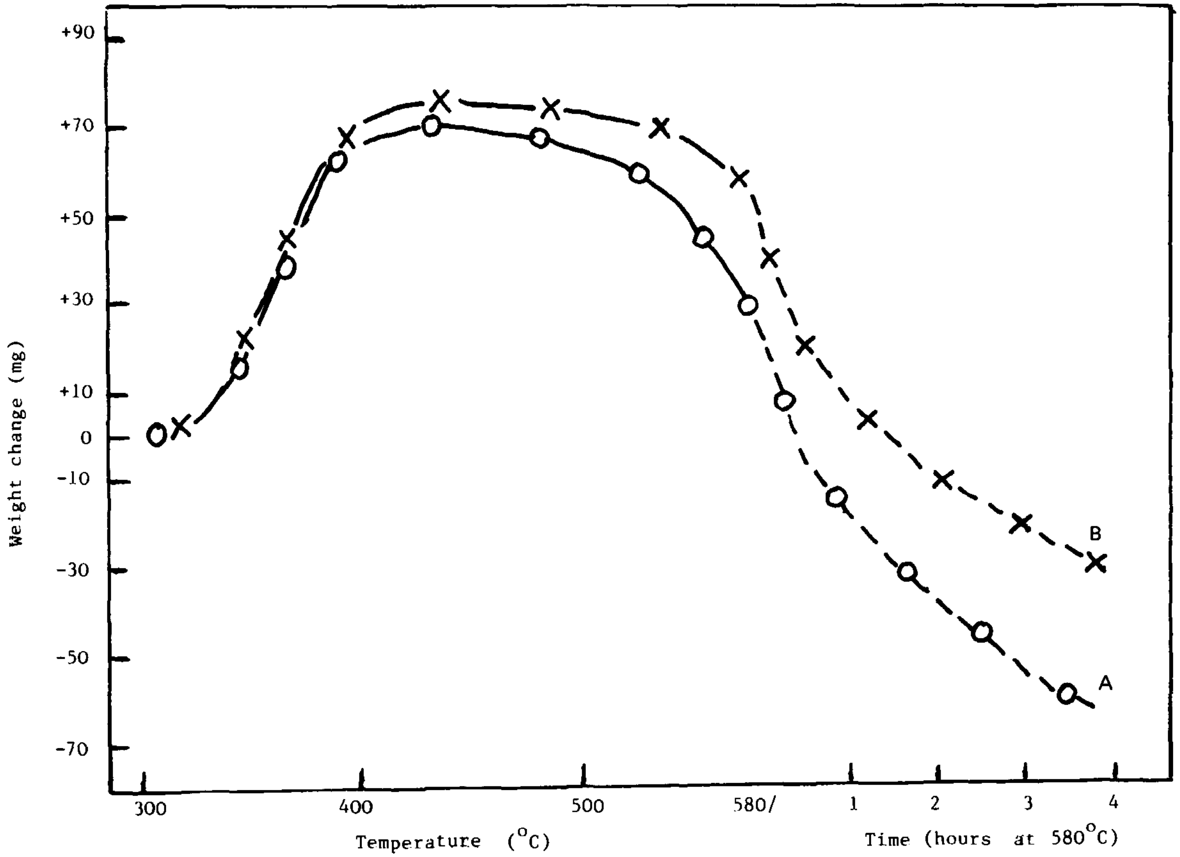

Fig. 4. Thermogravimetric analysis in ternary sulphate eutectic (3 g): curve A, ○, V_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (3.25 mmol.) (Expt. 12); curve B, ×, V_2O_5 (1.25 mmol.) + Nb_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (3.25 mmol.) (Expt. 13).

TABLE 3

V_2O_5 (1.35 mmol.) + Nb_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (6.5 mmol.) in ternary sulphate eutectic (3 g) heated under SO_2(10%)–N_2(30%)–air(60%) in gold crucibles

A.

Expt. no.	Wt. gain (mg) and temp. (°C)	Wt. loss to max. temp. (°C)	Wt. loss at max. temp. in time (m)	Total wt. loss	% V(IV) from $KMnO_4$ titn.	Calc. wt. gain from % V(IV)	Wt. of SO_3 in trap (mg)	Actual wt. change (mg)	Calc. wt. change (mg)
21	83(300–440)	12(580)	71(230)	83	81.5	81.1	146	0	−65
23	80(300–440)	10(580)	61(230)	71	81.5	81.1	?	+9	?
24	77(300–440)	16(580)	71(230)	87	81.4	81.0	116	−10	−35
46	86(310–430)	18(580)	69(230)	87	81.6	81.2	116	−1	−35
22	86(310–430)	12(560)	55 [a]	67	81.5	81.1	94	+19	−13

[a] Weight losses were 17 mg at 560 °C for 85 min, and 38 mg at 580 °C for 145 min.

B.

Expt. no.	Wt. gain (mg) and temp. (°C)	Wt. loss at max. wt. gain temp.	% V(IV) from $KMnO_4$ titn.	Calc. wt. gain from % V(IV)	Wt. of SO_3 in trap (mg)	Actual wt. change (mg)	Calc. wt. change (mg)
25	79(300–430)	13	89.5	89.1	34	+66	+55.5
26	77(300–430)	9	86.2	85.8	18	+68	+68
47	87(310–440)	11	87.4	87.0	26	+76	+61

TABLE 4

V_2O_5 (1.35 mmol.) + Nb_2O_5 (1.35 mmol.) + $K_2S_2O_7$ (6.5 mmol.) heated in ternary sulphate eutectic (3 g) under SO_2(6%)–N_2(56%)–air(38%)

Expt. no.	Wt. gain (mg) and temp. (°C)	Wt. loss to max. temp. (°C)	Wt. loss at max. temp. in time (m)	Total wt. loss	% V(IV) from $KMnO_4$ titn.	Calc. wt. gain from % V(IV)	Wt. of SO_3 in trap (mg)	Actual wt. change (mg)	Calc. wt. change (mg)
19	79(300–430)	to maximum weight gain			89.4	88.9	0	+79	+89
20	79(300–430)	to maximum weight gain			89.3	88.9	0	+79	+89
45	81(300–430)	10(580)	66(230)	76	83.6	83.2	120	+5	−37
17	83(300–430)	15(580)	45(105)	60	78.7	78.3	82	+23	−4

TABLE 5

V_2O_5 (1.35 mmol.) + Nb_2O_5 (1.35 mmol.) + $K_2S_2O_4$ (6.5 mmol.) in ternary sulphate melt (3 g) heated under air only (400 ml min^{-1})

Exp. no.	Wt. loss 380–580 °C (mg)	Wt. loss at 580 °C/230 min (mg)	Total wt. loss (mg)	% V(IV) from $KMnO_4$ titration	Wt. of SO_3 in trap (mg) and ratio of Col 6/4
28	14	40	54	20.6	45.6 (0.83)
34	15	45	60	19.2	50.4 (0.84)
40	12	39	51	20.4	38.4 (0.75)

10% mixture (Table 3), suggesting that sulphur dioxide partial pressure is not a very critical parameter, which is of course desirable in a catalyst system. Equation (4) still seemed to be applicable to the formation of vanadium(IV).

Finally, the effect of removing all sulphur dioxide was briefly investigated (Table 5). Here, surprisingly, about 20% vanadium(IV) was still present after 230 min at 580 °C, in contrast to mixtures without niobium(V) oxide when less than 10% vanadium(IV) was found [6], perhaps indicating that niobium stabilises the formation of a vanadium bronze under these conditions. The total weight loss was less than that found with sulphur dioxide present (Table 3A) but was significantly greater than the weight of sulphur trioxide trapped. This curiosity is probably linked with the absence of an external reducing agent to produce the vanadium(IV), which suggests a reaction similar to

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow 2VOSO_4 + 2SO_4^{2-} + \tfrac{1}{2}O_2 \qquad (5)$$

When melts containing niobium were solidified and dissolved in aqueous sulphuric acid, a gelatinous precipitate was formed in addition to the blue solution of vanadium(IV) customary from melts containing vanadium alone. This greenish-yellow precipitate, after filtration and heating to 430 °C for 5 min, gave X-ray powder diffraction lines (listed in ref. 9 and assigned to β-Nb_2O_5 with some $VOSO_4 \cdot 5H_2O$) and had a diffuse reflectance maximum at 13000 cm^{-1}, indicative of vanadium(IV). On thermogravimetric analysis of the precipitate, sulphur dioxide was lost at higher temperatures (520–860 °C) when the white solid formed gave a different X-ray diffraction pattern (now characteristic of $V_3Nb_{17}O_{50}$). This confirmed the volumetric results that most of the vanadium (96–99%) was leached out of the original gelatinous precipitate.

CONCLUSION

The apparent ability of niobium(V) (there was no evidence of lower oxidation states of niobium) to stabilise both vanadium(IV) (as a vanadium bronze) and vanadium(V) (as a V(V)–Nb(V)–$S_2O_2^{2-}$ polymer) is probably the origin of the promotion effect, as maintenance of the presence of both vanadium oxidation states in conditions which would normally favour more strongly one or the other oxidation state would probably enhance the catalytic activity.

The deduction of such interactions of complex melt–gas systems from comparatively simple thermogravimetric experiments suggests that similar procedures have much to contribute to the study of actual catalytic systems.

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