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A NEW MECHANISM FOR THE THERMAL DEGRADATION OF $BP \cdot 3H_2O$ WITH V_2O_5 AND TiO_2 SEMICONDUCTORS: A PHASE DIAGRAM STUDY

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ABSTRACT

The thermoanalytical behaviour of V_2O_5/TiO_2–$BP \cdot 3H_2O$ (BP = barium perchlorate trihydrate) binary systems were investigated under atmospheric pressure in the temperature range from ambient to 1050 °C. Using various molar ratios for each system, the TG, DTG and DTA graphs were obtained derivatographically. Several phases were identified for the system V_2O_5–$BP \cdot 3H_2O$. A phase diagram for the system solid $BaCl_2$–liquid ($BaCl_2 + V_2O_5$) was drawn to interpret the rather complicated XRD patterns obtained for some of the intermediate and final products. Both V_2O_5 and TiO_2 played the roles of catalysts in lowering the thermal dehydration and decomposition of $BP \cdot 3H_2O$ by about 40 and 60 °C, respectively. The E/n values for $BP \cdot 3H_2O$ alone and as the 2:1 molar ratio of $TiO_2:BP \cdot 3H_2O$ were found to be 156.2 and 105.7, respectively. The X-ray powder diffraction data for some intermediate and final products obtained in this study are given.

INTRODUCTION

V_2O_5 and TiO_2 have been shown to react with and catalyse the thermal decomposition of some peroxosalts such as alkali persulfates [1,2]. On the other hand, the thermal decomposition of halogen peroxosalts to produce oxygen for certain purposes was promoted with oxides [3–5]. Further, the thermal decomposition of $BP \cdot 3H_2O$ (BP = barium perchlorate trihydrate) was catalysed by β-MnO_2, Eu_2O_3 [6], Cr_2O_3 [7], La_2O_3 and Ni_2O_3 [8]. Acheson et al. [9] and Bansagt and Solymosi [10], studied the isothermal kinetics of the various decomposition steps of BP. The purpose of this paper is to investigate the thermoanalytical behaviour of the binary systems V_2O_5–$BP \cdot 3H_2O$ and TiO_2–$BP \cdot 3H_2O$.

EXPERIMENTAL

A MOM photorecording derivatograph was employed for registering TG, DTG and DTA curves simultaneously in a static air atmosphere. Two No. 3

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MOM platinum cylindrical crucibles without covers were used for sample and reference materials. Sample: 100 mg; heating rate: 10° min^{-1}. A Philips X-ray diffractometer with a copper target was used to obtain XRD patterns for intermediate and final products. The procedure is described elsewhere [11].

All chemicals used were of analytical grade (puriss) from Fluka AG, Buchs SG. α-Al_2O_3 sintered at 1300 °C was used as a reference material.

RESULTS AND DISCUSSION

Thermal behaviour of V_2O_5 and TiO_2

Figures 1 and 2 show that V_2O_5 is thermally stable up to the ceiling temperature of the program (1050 °C) with a slight loss of about 1 wt%, probably due to volatile impurities. Figure 2 indicates that TiO_2 loses less

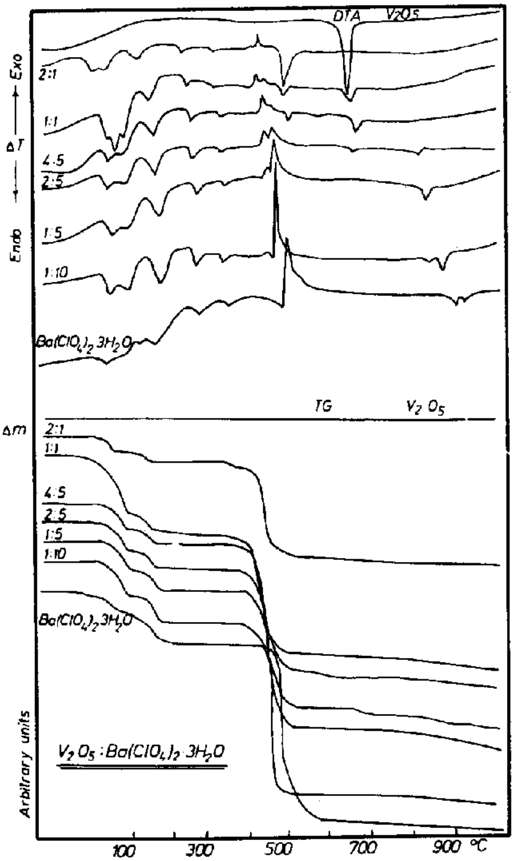

Fig. 1. TG and DTA curves for vanadium(V) oxide–barium perchlorate mixtures.

than 2 wt% at the end of the heating program. However, V_2O_5 gives a sharp endotherm at 670 °C, indicating the melting point of the oxide. The XRD patterns obtained for either oxide have been found to be similar to those of the ASTM cards [12,13] which advocate the formulae $(V_2O_5)_{14}$ and $(TiO)_6$ for the oxides.

The derivatographic behaviour of BP · $3H_2O$

Figure 1 shows the TG and DTA results for the thermal decomposition of BP · $3H_2O$ [9,10]. The final product is $BaCl_2$. The perchlorate loses moisture and one H_2O molecule up to 100 °C. The remaining two H_2O molecules are lost up to 200 °C. This occurs in two stages: at 100–145 °C, 0.5 H_2O is lost; at a later stage, 1.5 H_2O escape. Two endotherms then appear at 280 and 350 °C representing the crystalline phase transformation of anhydrous BP, which is thermally stable up to 455 °C (this plateau can be used for the gravimetric determination of BP). Thereafter, and up to 545 °C, BP loses about 33 wt% due to the liberation of oxygen gas. The loss occurs in four stages with a discontinuity leading to the formation [9,10] of barium chlorate (endo), chlorite (endo), hypochlorite (exo) and finally $BaCl_2$ (exo). Above 545 °C, no chemical change is seen. The DTA also shows two endotherms at 915, crystalline phase, and 940 °C, melting phase of $BaCl_2$. Experiments have shown that $BaCl_2$ prepared in this way has different XRD patterns to those mentioned in the ASTM cards; perhaps due to different modes of preparation or deviation in the lattice of the unit cell at higher temperatures. The *d*-spacings found were: 2.864, 5.433 and 3.690 Å (compare with ASTM cards 24-94 and 24-95).

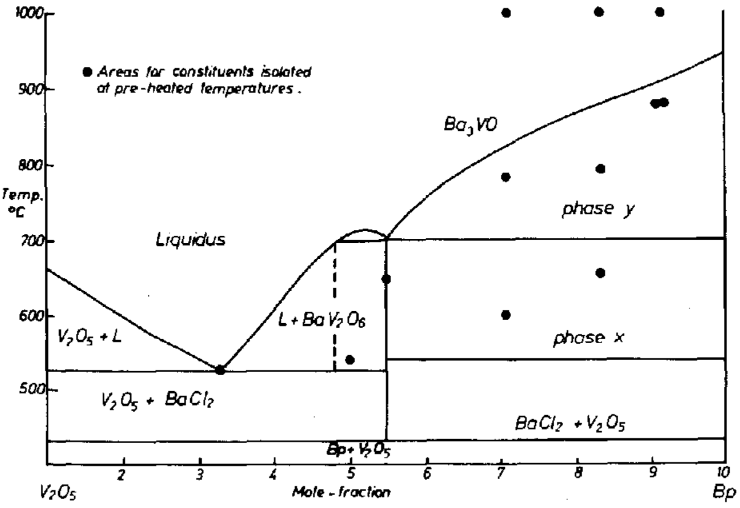

Fig. 2. Phase diagram of Bp–V_2O_5 binary system.

V_2O_5–BP · 3 H_2O system

Figure 1 shows the TG and DTA curves of various molar ratios of mixtures of the system V_2O_5–BP · $3H_2O$. A stepwise weght loss of BP starts at 400 and continues up to 545 °C. However, the DTA curve reveals two small endotherms representing two endothermic reactions which are followed by two unequal exotherms differing in height from one ratio to another. In the molar ratios 2 : 1, 1 : 1, 4 : 5 and 2 : 5, melting endotherms appear at 680 °C, probably attributable to the melting eutectic of the V_2O_5–salt mixture. The results obtained show that in all molar ratios the calculated O_2 gas liberated from the thermal decomposition of BP is less than that produced experimentally. This is also attributed to the liberation of gaseous chlorine, as in eqn. (1) below [12].

It is worth noting that the oxide could not shift the crystalline-phase changes of BP from their ordinary values: 280 and 350 °C.

In the molar ratios mentioned above, the oxide lowered the temperature of dehydration of the first and second molecules through catalysis, whereas the third one expelled at 180 °C. For the remaining molar ratios, where the amount of V_2O_5 is less, dehydration ends at 200 °C. The final products of the 1 : 10 sample were analysed by XRD, and this pattern showed, in addition to the $BaCl_2$ *d*-lines, important *d*-spacings at 3.045, 3.129 and 3.166 Å, which are very close to the *d*-spacings of the compound Ba_3VO [13]. On the other hand, the typical endotherms of $BaCl_2$ were shifted to 855 and 880 °C. The first endotherm became larger and sharper indicating the formation of a melting eutectic mixture.

The thermal reaction products of the 1 : 5 sample at 650, 790 and 1000 °C were analysed by XRD. All XRD patterns thus obtained indicate [14] the presence of Ba_3VO. In addition to this compound, an unknown phase having bright *d*-spacings of 3.500, 2.010 and 1.760 Å was formed at 790 °C. Similarly, at this ratio $BaCl_2$ showed a melting endotherm at 850 °C. Almost identical products were obtained with the 2 : 5 sample when heated at 650 (pink), 790 (pale yellow) and 1000 °C (white). Differences in the colour of the solids could be ascribed to defective crystalline structures resulting from the different thermal histories of the samples isolated [15].

Samples of molar ratio 4 : 5 heated to 515, 550 and 600 °C gave XRD patterns of a mixture of unreacted V_2O_5, BaV_2O_6 and $BaCl_2$. At 550 °C, the product consisted mainly of BaV_2O_6, with a little $BaCl_2$. Almost identical products were found for samples isolated at 660 °C. The endotherm at 710 °C represents the melting of BaV_2O_6. This compound was found in the 1 : 1 samples heated to 530 °C. However, the melting eutectic of the compound was shifted to 700 °C.

The 4 : 5, 1 : 1 and 2 : 1 samples exhibited melting eutectic endotherms of various areas at 520 °C, indicating a reaction between molten V_2O_5 and $BaCl_2$ to form BaV_2O_6 where the $BaCl_2$ endotherms completely disappeared from the DTA curve.

Phase diagram study

The melting and solubility relationships of multi-component systems as a function of temperature can be described by their phase diagrams. In suitable cases, the diagram may be obtained from DTA curves, such as those shown in Fig. 1. As is evident from Table 1, it is possible to calculate mole fractions for components of different molar ratios. Actually, a phase diagram is a quantitative diagram which shows mole fractions of a constituent versus temperature. The aim of the construction of this phase diagram (Fig. 2) is to account for the appearance of XRD patterns for some complicated phases of intermediates and final products formed as solid–liquid phases during the thermal processes. Here, solid immiscible $BaCl_2$ represents mainly the solid phase for all molar ratios prepared, whereas the liquid phases consist of molten mixtures equilibrated with BaV_2O_6 and other unknown phases, i.e., phases x and y in addition to phase Ba_3VO [16].

A new mechanism

It is well known that V_2O_5 in acid chloride solutions acts as a catalyst as well as a strong oxidising agent, because of the formation of the VO_2^+ ion. It has been found that V_2O_5 lowers the initial decomposition of BP by about 60 °C through catalysis. Also, it has been shown that the oxide reacts in the molten state with $BaCl_2$ to form BaV_2O_6, thus liberating Cl_2 gas. A mechanism for the above reaction could be suggested as follows

$$V_2O_5(l) + BaCl_2(s) + 0.5O_2(g) \xrightarrow[670\,^\circ C]{air} BaV_2O_6(l) + Cl_2(g) \tag{1}$$

TiO_2–$BP \cdot 3H_2O$ system

TiO_2, being chemically and catalytically active, reacts at high temperatures with alkali persulfates [1] to form the sulfate and double salts. To

TABLE 1

Melting points and mole fractions for different molar ratios of the V_2O_5–$BP \cdot 3H_2O$ system

Molar ratio (Oxide : BP)	Mole fraction		Melting point			Compound isolated at		
	$BP \cdot 3H_2O$	V_2O_5	V_2O_5	$BaCl_2$	Product	530–660 °C	780–790 °C	1000 °C
0:1	1	0	–	940	–			
1:0	–	1	670	–	–			
1:10	0.900	0.100	–	880	–			Ba_3VO
1:5	0.833	0.166	–	850	–	Phase x	Phase y	Ba_3VO
2:5	0.714	0.283	–	840	–	–	–	–
4:5	0.555	0.444	–	700	525	BaV_2O_6	–	–
1:1	0.500	0.500	–	700	525	BaV_2O_6	–	–
1:2	0.333	0.666	–	–	525	The product is fused		

TABLE 2

The effect of TiO_2 on the thermal decomposition of barium perchlorate trihydrate

Molar ratio (oxide : BP)	Weight %		Phase change, T °		Decomp. of BP		$BaCl_2$, T	Second reaction, T_i
			T_1	T_2	T_i	T_f		
2 : 1	29.0	71	280	350	420	535	915	800
1 : 1	17	83	280	350	420	540	915	800

examine the effect of TiO_2 on the thermal decomposition of a halogen peroxosalt such as $BP \cdot 3H_2O$, the molar ratios 1 : 1 and 1 : 2 of $TiO_2 : BP \cdot 3H_2O$ were chosen. Figure 3 shows the TG and DTA curves recorded for these two ratios. Table 2 indicates that the oxide could lower the thermal decomposition temperature (T_i) of BP by about 40 °C. The two endotherms which belong to the crystalline-phase change of BP at 280 and 350 °C do not change. The oxide could also catalytically lower the thermal decomposition temperatures of the first and second H_2O molecules, and by about 100 °C, and the third H_2O molecule by about 20 °C. Between 545 and 800 °C a

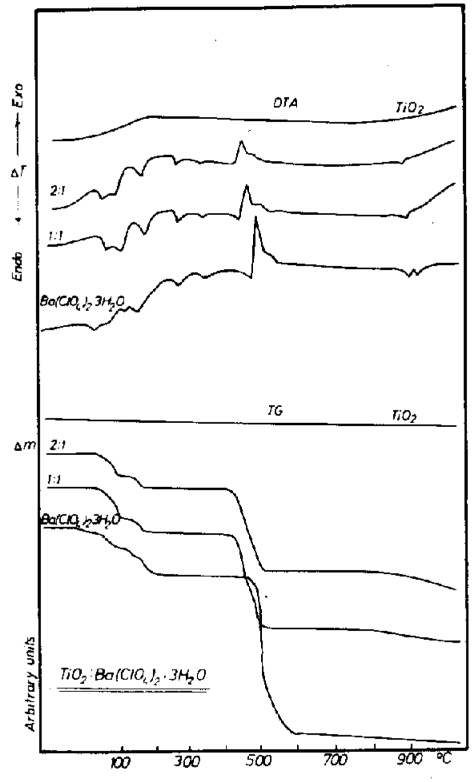

Fig. 3. TG and DTA curves for titanium(IV) oxide–barium perchlorate mixtures.

plateau is formed. The horizontal plateau then descends gradually where the oxide either reacts with $BaCl_2$ or loses some of its oxygen, and the Ti : O ratio becomes less than the stoichiometric value; this is indicated by the disappearance of the XRD pattern of TiO_2 and the formation of an unknown species of *d*-spacings 3.424, 3.240 and 3.230 Å, where $I/I_0 =$ 50–100%. This pattern could be matched with those of any compound mentioned in the ASTM cards, probably due to the incomplete formation of barium titanate, $BaTiO_2$, which needs a few hours of isothermal heating and higher temperatures (~ 1450 °C) for its completion. However, its DTA curve showed no changes in the enthalpy of the system due to losses of O_2 or Cl_2 gases which indicates the formation of barium titanate, although the disappearance of the melting endotherm of $BaCl_2$ at 940 °C suggests the possibility of its exothermic reaction with TiO_2.

TiO_2–$BaCl_2 \cdot 2\ H_2O$ system

To examine the chemical and catalytic reactivity of TiO_2 towards $BaCl_2 \cdot H_2O$ over the temperature range from ambient to 800 °C, barium chloride dihydrate was prepared derivatographically by heating BP · H_2O to 620 °C.

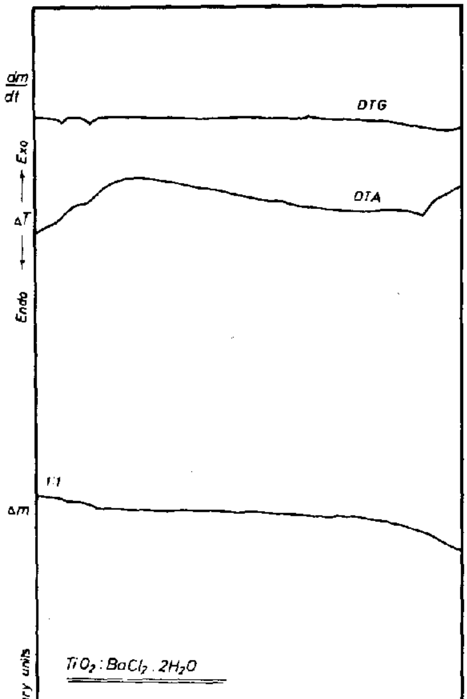

Fig. 4. TG, DTG and DTA curves for titanium dioxide–barium chloride mixture.

The resulting chloride was then cooled, mixed with TiO_2 in the molar ratio 1 : 1, and an appropriate amount was subjected to the heating program (Fig. 4). Careful sruntiny of the figure reveals that anhydrous $BaCl_2$ on cooling could absorb $2H_2O$ to form the hydrated salt, which of course loses these two molecules in two steps [17]. However, in the presence of TiO_2, the first H_2O molecule was expelled at 60 °C, and the second at 120 °C (in contrast with the absence of TiO_2 where it loses the first H_2O molecule at > 60 °C, and the second at 160 °C). This means that catalysis could lower the expulsion temperature of the second H_2O molecule by 40 °C. After 120 °C, the TG curve remained horizontally stable until 800 °C, when it started to fall. The XRD patterns for final products of this and the above-mentioned systems were found to be identical.

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