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THERMAL DECOMPOSITION OF VANADIUM OXYSALTS

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ABSTRACT

The study of the thermal decomposition of $V_2(SO_4)_3$, $VOSO_4 \cdot 5\,H_2O$, $VO(CH_3$-$COO)_2$ and $VOC_2O_4 \cdot 2\,H_2O$ has been made in argon and hydrogen atmospheres and compared with that in air by following thermogravimetry and differential thermal analysis. The decomposition products are characterized by chemical analysis, IR, and X-ray powder diffraction methods. The results suggest that all the salts decompose to V_2O_5 in air and to V_2O_3 in hydrogen. In argon atmosphere, the sulphates decompose to V_2O_5 whereas the carboxylates decompose to V_2O_3.

INTRODUCTION

The study of the thermal behaviour of transition metal oxycompounds is of special interest due to the formation of various oxides during the decomposition [1,2]. The desired oxides are generally obtained by the temperature programme heating under different atmospheres. The reduction of metal sulphates gives rise to various products such as lower valent sulphates, metals, sulphides, oxides or a mixture of oxide and sulphide [3,4]. Although it is reported [5] that $VOSO_4 \cdot 5\,H_2O$ decomposes in air to give V_2O_5, the precise temperature has not been determined. Vanadium pentoxide is also obtained as the final product of decomposition of vanadyl acetate [6] and vanadyl oxalate [7] in air, though VO_2 is found to be the transient phase. Reported in this paper are the thermogravimetric and differential analysis studies of $V_2(SO_4)_3$, $VOSO_4 \cdot 5\,H_2O$, $VO(CH_3COO)_2$ and $VOC_2O_4 \cdot 2\,H_2O$ in atmospheres of air, argon and hydrogen. The decomposition residues are characterized by wet chemical analysis, IR spectral measurements and X-ray powder diffraction patterns.

EXPERIMENTAL

The vanadyl sulphate pentahydrate was commercially available reagent grade. $V_2(SO_4)_3$ was prepared by the reduction of V_2O_5 in H_2SO_4 using elemental sulphur [8]. $VO(CH_3COO)_2$ was obtained by the solvolysis of VCl_5 in acetic anhydride [9], and vanadyl oxalate dihydrate was prepared [7] by the interaction of V_2O_5 and oxalic acid. Vanadium(V) and the lower valent vana-

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dium were determined by potentiometric method employing Fe(II) and Ce(IV) reagents [10].

TG and DTA studies were made using a Stanton thermobalance, Netzsch differential thermal analyzer and a Mettler simultaneous TG—DTA analyzer. Samples were linearly heated at the rate of 6°C min^{-1} under a flow stream of argon and hydrogen. The IR spectra of the decomposition products were measured with Perkin-Elmer 257 and Polytec IR 30 Fourier spectrometers. The X-ray powder patterns were obtained using CuK_α radiation.

RESULTS AND DISCUSSION

TG and DTA results of $V_2(SO_4)_3$, $VOSO_4 \cdot 5\,H_2O$, $VO(CH_3COO)_2$ and $VOC_2O_4 \cdot 2\,H_2O$ in argon atmospheres are given in Figs. 1 and 2. As can be seen from the TG curve, $V_2(SO_4)_3$ decomposes in a single step in the temperature range 450—620°C, with a weight loss of 53.0% which corresponds to the calculated weight loss of 53.4% for the formation of V_2O_5. The DTA curve shows an endotherm at 600°C corresponding to the decomposition of the sulphate moiety. The sharp endotherm at 680°C is reversible in that an exotherm is obtained on cooling at 660°C. The melting of V_2O_5 is reported [11] at 690°C so the endothermic peak at 680°C is ascribed to this effect. The brown residue obtained was found to be fused and wet chemical analysis verified it to be vanadium(V) oxide. The IR spectrum exhibited bands at (cm^{-1}) 1017s, 825s, 590s, b, 380m, 290s and 220m, characteristic of V_2O_5 [12,13]. Further, the X-ray powder patterns of the residue gave d_{hkl} values (Å) 5.75m, 4.39s, 4.05m, 3.35s, 2.87s, 2.73m, 2.59m, 2.19w, 1.98w, 1.91m, 1.76m which correspond well with those of V_2O_5 [14].

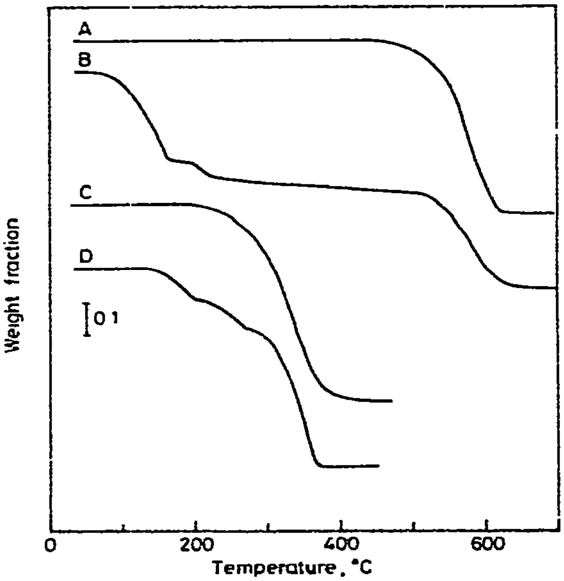

Fig. 1. TG plots of $V_2(SO_4)_3$ (A), $VOSO_4 \cdot 5\,H_2O$ (B), $VO(CH_3COO)_2$ (C), and $VOC_2O_4 \cdot 2\,H_2O$ (D).

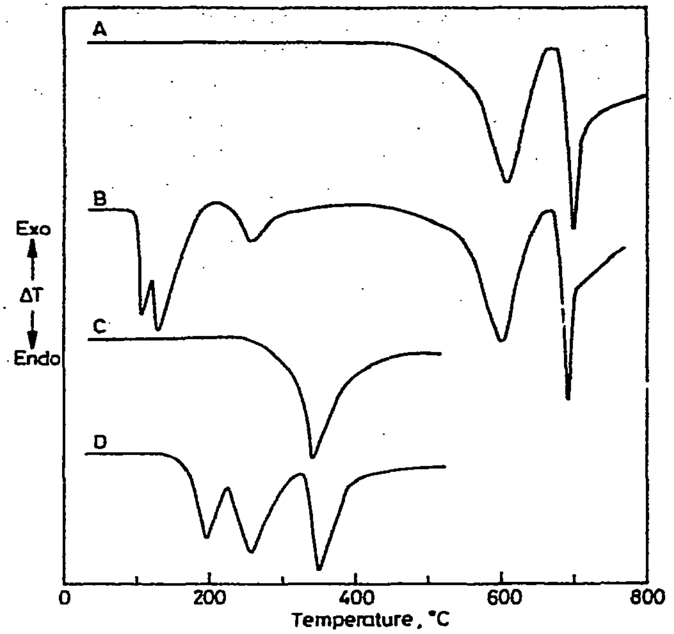

Fig. 2. DTA plots of $V_2(SO_4)_3$ (A), $VOSO_4 \cdot 5\ H_2O$ (B), $VO(CH_3COO)_2$ (C), and $VOC_2O_4 \cdot 2\ H_2O$ (D).

The thermal plots in hydrogen atmosphere showed that $V_2(SO_4)_3$ decomposes with a weight loss of 61.0% (expected value for V_2O_3 formation 61.6%) in the temperature range 450—650° C, with an endothermic maximum at 600° C. The final product was black and chemical analysis showed it to be vanadium(III) oxide. The IR spectrum gave bands at (cm^{-1}) 985w, b, 520w, 420w and 370w which are attributed to V_2O_3 [15]. The X-ray powder patterns exhibited d_{hkl} values (Å) 3.63s, 2.70s, 1.47m, 1.33m, characteristic of V_2O_3 [16]. The thermal behaviour of $V_2(SO_4)_3$ in air is found to be similar to that observed in argon atmosphere, indicating that air does not influence its decomposition. The decomposition scheme is thus represented as

$$V_2(SO_4)_3 \xrightarrow{\text{Air/argon}} V_2O_5 + 3\ SO_2 + 0.5\ O_2$$

$$V_2(SO_4)_3 + 3\ H_2 \rightarrow V_2O_3 + 3\ SO_2 + 3\ H_2O$$

The TG plot of $VOSO_4 \cdot 5\ H_2O$ in argon shows that there are three distinct stages of decomposition: the corresponding temperatures are 80—160, 200—350 and 460—620° C. The weight loss associated with the first stage is 28.0% which corresponds with the theoretical value of 28.5% for the removal of four molecules of water of hydration. The second stage is accompanied by a further weight loss of 7.0% due to the formation of $VOSO_4$. On exposure to the atmosphere the anhydrous product gradually regained weight to reform the pentahydrate. The final stage of decomposition is accompanied by the weight loss leading to an overall value of 64.0% at 620° C which is in excellent agreement with the value of 64.1% expected for V_2O_5 formation. The

DTA curve shows endothermic peaks at 105, 125 and 250° C due to dehydration, a peak maximum at 600° C attributed to the formation of V_2O_5, and that at 680° C due to the melting of V_2O_5. As in the case of $V_2(SO_4)_3$, the thermal plots of $VOSO_4 \cdot 5\ H_2O$ in air and argon are quite similar. In hydrogen atmosphere, after the stepwise dehydration, the anhydrous $VOSO_4$ formed decomposes in a single step in the temperature range 450—650° C, registering a total loss of 70.0% weight which corresponds to the formation of V_2O_3. Chemical, IR and X-ray analyses of the products confirmed that in air and argon atmospheres V_2O_5 is formed, and in hydrogen atmosphere the product is V_2O_3. The reaction scheme of anhydrous vanadyl sulphate decomposition can be written as

$$2\ VOSO_4 \begin{array}{l} \xrightarrow{\text{Air/argon}} V_2O_5 + 2\ SO_2 + 0.5\ O_2 \\ \xrightarrow[H_2]{} V_2O_3 + 2\ SO_2 + 3\ H_2O \end{array}$$

$VO(CH_3COO)_2$ decomposes in a single step in argon atmosphere in the temperature range 220—360° C, with a loss of 59.0% which corresponds to the expected value of 59.5% for the formation of V_2O_3. The DTA curve shows an endothermic peak at 340° C. The decomposition in hydrogen atmosphere was apparently similar to that in argon atmosphere. However, in air the TG curve shows a slight increase in weight during the final stages of the reaction. The weight loss observed at 360° C is found to be 59.5% which agrees very well with the calculated weight loss of 50.8% for the formation of V_2O_5. The DTA curve exhibited an endotherm at 340° C followed by a small exotherm at 360° C. It has been reported [6] that during the decomposition in air, $VO(CH_3COO)_2$ gives rise to VO_2 and the increase in weight in the TG curve and the exotherm in the DTA curve are attributed to the oxidation process of VO_2 to V_2O_5. The chemical, IR and X-ray measurements of the residues confirmed the presence of V_2O_5 in air and V_2O_3 in inert and reducing atmospheres.

Vanadyl oxalate dihydrate loses weight in argon atmosphere (Fig. 1D) in three stages. The first stage takes place between 100 and 200° C with a loss of 9.0% weight corresponding to the removal of a molecule of water of crystallization. The second molecule of water is lost in the temperature range 220—280° C, registering a total loss in weight of 18.5% which agrees very well with 18.9%, the calculated value for the formation of VOC_2O_4. The anhydrous oxalate decomposes in the temperature range 300—380° C, losing an overall mass of 60.0% which corresponds to the value of 60.8% calculated for the formation of V_2O_3. The DTA showed endothermic peaks at 120 and 260° C due to the dehydration and an endotherm at 350° C attributed to the decomposition of the oxalate moiety. The results of the product analysis confirmed it to be V_2O_3. On exposure to the atmosphere the anhydrous oxalate rehydrates, indicating that it is an unstable phase. The nature of decomposition in hydrogen atmosphere is similar to that found in argon, suggesting that hydrogen does not influence the reduction process of the oxalate. However, in air, after the dehydration stage VOC_2O_4 decomposes with an overall weight loss of 52.0% which corresponds to 52.4% calculated for

V_2O_5 formation. The DTA curve showed, in addition to the endothermic peak, an exotherm at 340°C and there was an indication of weight gain in the TG curve at the final stages of decomposition. These observations are attributed [7] to the oxidation of VO_2 to V_2O_5.

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