

THERMAL STUDIES OF THE REACTIONS OF VANADIUM(V) OXIDE WITH OTHER TRANSITION METAL OXIDES

D. J. HUCKNALL* and C. F. CULLIS

Department of Chemistry, The City University, London, U.K.

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Studies of the thermal behaviour of binary oxide mixtures containing vanadium(V) oxide (V_2O_5 - TiO_2 , V_2O_5 - MoO_3 , V_2O_5 - ZrO_2 and V_2O_5 - ZnO) have shown that the evolution of gaseous oxygen at fairly low temperatures is characteristic of those systems which are effective catalysts for the oxidation of hydrocarbons. No weight changes were observed with V_2O_5 - ZnO mixtures under these conditions and, in accordance with this, zinc(II) oxide does not enhance the catalytic activity of vanadium(V) oxide. In V_2O_5 -containing systems, evolution of oxygen occurs during the reduction of V_2O_5 to V_2O_4 . This process is accelerated in the presence of certain metal oxides and such acceleration may be caused by structural interactions at the interface of the oxides. Among the systems studied, the formation of compounds such as $Mo_6V_9O_{40}$ is thought to be of little significance from the catalytic point of view.

Vanadium(V) oxide is a well-established catalyst for the partial oxidation of hydrocarbons [1]. In the presence of other metal oxides, however, higher activities and selectivities can be achieved. The dependence of the catalytic efficiency of solid V_2O_5 -containing systems on physicochemical properties is not fully understood, although detailed studies have been made with binary mixtures, some of which are known to form the basis of effective catalysts for the selective oxidation of hydrocarbons. Such systems include V_2O_5 - TiO_2 [2-4], V_2O_5 - MoO_3 [5-8], V_2O_5 - SnO_2 [9] and V_2O_5 - CoO [9]. In certain cases, the formation of compounds such as TiV_4O_{12} [10], $Mo_6V_9O_{40}$ [6, 8] and $Co_2V_2O_7$ [11] has been observed during the high-temperature, solid-state reactions of binary oxide mixtures, although it is not clear to what extent such mixed oxides are involved in catalytic oxidation processes.

This paper reports the thermal behaviour (studied by differential thermal analysis (DTA) and thermogravimetry (TG)) of some V_2O_5 -transition metal oxide systems. Some of these findings have been briefly mentioned elsewhere in connection with other physicochemical measurements on these systems [2, 5], but it was felt that the results of the thermal studies merited more detailed description.

* Present address: J. and S. Sieger Limited, Poole, Dorset, U.K.

Experimental

Vanadium(V) oxide, molybdenum(VI) oxide, zirconium(IV) oxide and zinc(II) oxide were of AnalaR quality or of the highest purity available and were used without further purification. Vanadium(V) oxide was also prepared by the thermal decomposition of AnalaR ammonium metavanadate. Titanium(IV) oxide (both anatase (Tiona G) and rutile (Runa RG) modifications) was supplied by Laporte Industries Ltd., and X-ray diffraction revealed the presence of no other phases. Titanium(IV) oxide, as brookite, was supplied by Tioxide International and contained at least 97% TiO_2 . Oxide mixtures were usually prepared by mechanically grinding the constituent oxides, in the desired proportions, as a slurry in acetone until the mixture was homogeneous. The product was then dried in air at 100° .

Isobaric weight-change and differential thermal analysis measurements were carried out on a Mettler Thermoanalyser II thermobalance. The minimum detectable weight change for 50–100 mg samples was 2×10^{-5} g and for DTA, a maximum sensitivity of 5×10^{-7} V (f.s.d. 2×10^{-5} V) was observed. Thermal analysis was carried out in flowing atmospheres of nitrogen, oxygen and of mixtures thereof, and of hydrogen. A 16 mm diameter platinum crucible was used in TG experiments involving nitrogen or oxygen atmospheres, whilst a 16 mm diameter silica crucible was required for determinations in a hydrogen atmosphere. It was observed that, within 1–2%, variation of the sample size up to 200 mg had scarcely any effect on the weight change. In the DTA experiments, samples of ca. 40 mg were placed in 6 mm diameter platinum crucibles and α -alumina was used as the reference material.

In order to identify the products of any solid state reaction, X-ray diffraction studies were carried out using a Philips PW 1010 diffraction apparatus and nickel-filtered CuK_α radiation. Samples to be analysed were reduced in an agate mortar before being placed in a Philips powder camera (1.146×10^{-1} m diameter), in which the samples could be rotated. A computer program was written in order to calculate the necessary results from the diffraction patterns. Hot-stage X-ray diffraction studies were carried out using CuK_α radiation with the sample held on a platinum grid located inside a Lenné camera (1.154×10^{-1} m diameter). The sample was heated from room temperature to 1100° at a rate of 10^{-2} s $^{-1}$.

Results

1. Vanadium(V) oxide – titanium(IV) oxide

(i) V_2O_5 – anatase

Mixtures covering the composition range 100% V_2O_5 to 100% TiO_2 were prepared and thermogravimetry was performed in flowing nitrogen or oxygen at a heating rate of 1°min^{-1} . No weight changes were observed below 600° . At temperatures above 600° , however, a gradual decrease in weight was observed

for samples containing both components; the loss in weight was complete at 700°. Mass spectrometric analysis showed that oxygen was evolved during heating, and that this originated exclusively from the vanadium(V) oxide.

Figure 1 shows the variation with temperature of the weight loss (expressed as a percentage of the original weight) from a mixture containing 25% w/w V_2O_5 . For example, a 100 mg sample, when heated continuously to 700°, lost 1.36 mg between 615 and 690°. Variation of the heating rate had no effect on the weight lost from a particular sample and did not alter the temperature range over which the weight loss occurred. The observed behaviour was also independent of the source of the two constituent oxides.

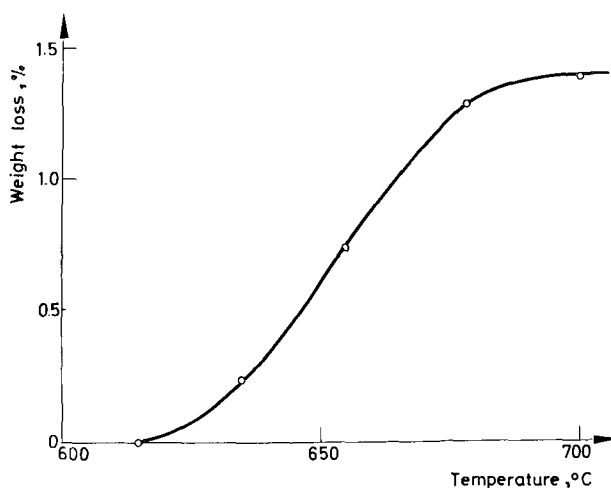


Fig. 1. The variation of weight loss with temperature for a vanadium(V) oxide (25% w/w) — titanium(IV) oxide (anatase) mixture heated in air.

The magnitude of the weight loss was found to vary with mixture composition and with the oxygen-content of the surrounding atmosphere [2]. In both cases, the maximum weight loss was observed at about 25% w/w V_2O_5 . Neither anatase nor pure vanadium(V) oxide changed weight in this temperature range, although the latter compound was found to lose weight continuously when heated above 750° in nitrogen and, to a lesser extent, in oxygen. The rate of loss of weight under these conditions was found to increase with temperature. Samples containing vanadium(V) oxide and anatase also lost weight when heated above 800° but the thermal analysis traces were similar to that of V_2O_5 alone and there were no other significant weight changes when samples were heated to 1020°C.

Figure 2 shows the variation of weight loss with oxygen content of the surrounding atmosphere. During these studies, it was also found that samples, which had been heated to 700° in oxygen and cooled to room temperature, did not lose

more weight when re-heated to 700° in nitrogen and that samples previously heated in nitrogen did not gain weight when re-heated in oxygen.

Thermal analysis was also carried out in hydrogen. A weight loss was observed between 500 and 700° and this occurred in two stages. The variation of weight loss with composition for samples previously heated in nitrogen to 600° revealed that the weight lost from each sample increased linearly with increasing V_2O_5 content. However, for those samples which had previously been heated to ca. 700° in nitrogen, the curve was not linear (Fig. 3).

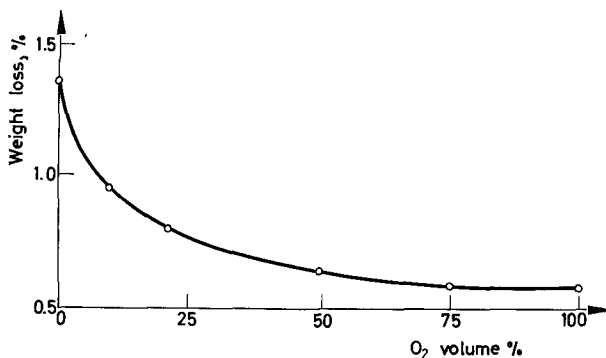


Fig. 2. The variation of weight loss with oxygen content of the surrounding atmosphere for a vanadium(V) oxide (25% w/w) — titanium(IV) oxide (anatase) mixture heated to 700°.

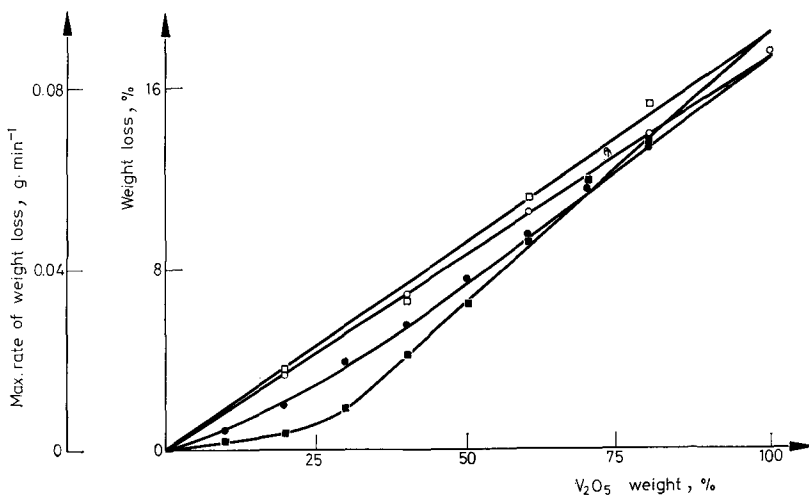


Fig. 3. The variation of weight loss (circles) and maximum rate of weight loss (squares) with composition of vanadium(V) oxide — titanium(IV) oxide (anatase) mixtures heated to 750°C in hydrogen. ○, □, samples previously heated to 600° in air; ●, ■, samples previously heated to 750° in nitrogen.

Figure 4 shows thermal analysis traces for samples containing 10%, 25%, 40% and 80% w/w V_2O_5 heated at 4° min^{-1} in nitrogen. The DTA trace for a mixture containing 10% w/w V_2O_5 shows a broad endothermic peak in the temperature range in which the weight loss occurs, the maximum coinciding with the maximum rate of weight loss (Fig. 4(a)). The trace for a mixture containing 25% w/w V_2O_5 shows a similar peak occurring as a shoulder on a second peak at 695° , which

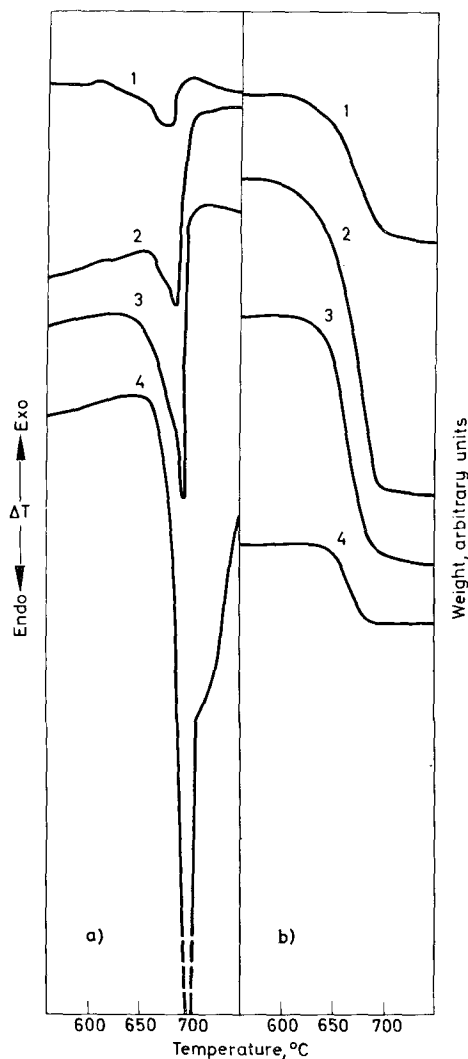


Fig. 4. Differential thermal analysis and thermogravimetry of vanadium(V) oxide — titanium (IV) oxide (anatase) mixtures. (a) DTA curves; (b) TG curves. 1. 10% w/w V_2O_5 ; 2. 25% w/w V_2O_5 ; 3. 40% w/w V_2O_5 ; 4. 60% w/w V_2O_5 .

corresponds to the melting point of vanadium(V) oxide. The traces for samples containing 40% and 80% w/w V_2O_5 are similar to that containing 25% w/w V_2O_5 , the peak at 695° increasing in size as the concentration of V_2O_5 increases. The TG traces (Fig. 4(b)) also show clearly that the weight loss occurs immediately before the melting of the vanadium(V) oxide. The DTA results are summarised in Table 1.

Vanadium(V) oxide–anatase mixtures were analysed by X-ray diffraction before, during, and after the loss in weight. Comparison of the results with those for V_2O_5 -rutile mixtures showed that all the diffraction lines present could be ascribed to these two compounds. This indicates that, when a vanadium(V) oxide–anatase mixture is heated to 700°, a phase-change (anatase → rutile) occurs and no intermediate compound exists in the cooled sample. Further, the X-ray diffraction pattern of a previously unheated sample containing 25% w/w V_2O_5 was determined by means of a hot-stage X-ray diffraction camera, in which the sample was heated from room temperature to 1100°. The phase-change in the region of 700° was easily observed and all the diffraction lines present at higher

Table 1
DTA results for some V_2O_5 – TiO_2 mixtures

| Initial composition | Atmosphere | Appearance of DTA peaks | Extrapolated onset temperature, °C | Temperature interval for weight change, °C |
|--------------------------------|------------|---|------------------------------------|--|
| 10% w/w V_2O_5 – anatase | N_2 | Small exotherm Complex double endotherm | 605 626, 665 | 611–714 |
| 25% w/w V_2O_5 – anatase | N_2 | Small exotherm Double endotherm Exotherm | 585 665, 674 690 | 615–691 |
| 30% w/w V_2O_5 – brookite | N_2 | Broad endotherm Sharp endotherm | 623 673 | 603–705 |
| | O_2 | Sharp endotherm Sharp endotherm Broad endotherm | 657 673 | 2 stages (i)635–689 (ii)689–725 |
| 40% w/w V_2O_5 – anatase | N_2 | Double endotherm Exotherm | 650, 678 683 | 603–708 |
| 80% w/w V_2O_5 – anatase | N_2 | Small exotherm Endotherm | 583 673 | 627–683 |

In all cases the endothermic processes coincide with the loss of oxygen from the mixtures and the melting of vanadium(V) oxide.

temperatures could be ascribed to either vanadium(V) oxide or rutile. Above 700°, however, most of the lines due to V₂O₅ were absent. Owing to the design of the hot-stage X-ray camera, however, it was not possible to determine whether the phase-change occurred gradually or suddenly.

Mixtures containing 25% w/w V₂O₅ were therefore heated to intermediate temperatures in the weight-loss region and then analysed by X-ray diffraction. Lines due to both anatase and rutile were present in the patterns of those samples heated between 600 and 700° (i. e. before weight loss was complete). As the temperature was increased, however, the lines due to rutile increased in intensity, samples heated to 700° showing patterns for titanium(IV) oxide exclusively as the rutile phase. Finally, X-ray diffraction patterns were obtained for vanadium(V) oxide-anatase mixtures covering the whole composition range and heated to 700° in nitrogen and oxygen. Particularly significant is the fact that phase-transformation was never complete, unless mixtures contained at least 25% w/w V₂O₅.

Studies of the thermal behaviour of mixtures containing either V₂O₄ or V₂O₃ and anatase showed that no weight changes occurred when such mixtures were heated to 1000° in nitrogen. In the presence of oxygen, a weight gain was observed between 250 and 500° for samples containing V₂O₄ and between 200 and 550° for the corresponding mixtures containing V₂O₃. Thereafter, a weight loss took place between 610 and 690°. The weight changes were consistent with the occurrence of the reactions:



At the appropriate temperatures and were followed by evolution of oxygen, typical of vanadium(V) oxide-anatase mixtures. X-ray diffraction studies showed that, after being heated to 1000° in nitrogen, samples containing V₂O₄ and V₂O₃ contained titanium(IV) oxide only as anatase. Similar results were obtained for samples heated to 550° in oxygen, although for samples heated to 750° in oxygen, rutile was the only TiO₂ phase present.

(ii) V₂O₅-brookite

Thermal analysis of vanadium(V) oxide-brookite mixtures was carried out in nitrogen and oxygen. The magnitude of the weight loss in both gases was found to vary with mixture composition, the maximum weight loss occurring with mixtures containing ca. 30% w/w V₂O₅ [2]. As regards the magnitude of the maximum weight losses, 100 mg samples lost ca. 1.8 wt % in nitrogen and ca. 0.7 wt % in oxygen. Although the thermal behaviour in nitrogen was similar to that of vanadium(V) oxide-anatase mixtures, the behaviour in oxygen was quite different. For a sample containing 30% w/w V₂O₅ heated in nitrogen, a single weight loss occurred between 600 and 700°. The DTA trace (Table 1) showed two endothermic peaks. The first, at 650° (extrapolated onset temperature, 623°),

was small and broad, whilst the second, at 685° (extrapolated onset temperature, 673°), was much sharper. In contrast, a similar sample heated in oxygen showed a two-stage weight loss. The first loss occurred between 610 and 660° and the second between 700 and 730°. The corresponding DTA trace showed three endothermic peaks having extrapolated onset temperatures at 657, 673 and 705° respectively.

Vanadium(V) oxide—brookite mixtures were analysed by means of X-ray diffraction, before and after being heated in nitrogen and after the first and second weight losses in oxygen. Mixtures heated to 600° in nitrogen and oxygen were found to contain V_2O_5 and brookite only. In the case of a sample containing 30% w/w V_2O_5 heated to 700° in nitrogen, all the diffraction lines present could be ascribed to vanadium(V) oxide and rutile. These results suggest that such thermal treatment converts brookite directly into rutile without the formation of an intermediate compound. For a sample containing 30% w/w V_2O_5 heated to 690° in oxygen (after the first weight loss), comparison of the X-ray diffraction data with those for a corresponding V_2O_5 —anatase mixture showed that all the lines could be ascribed to the two constituent oxides. Diffraction studies on a similar sample heated to 750° in oxygen showed that titanium(IV) oxide was present exclusively as rutile.

(iii) V_2O_5 —rutile

Binary mixtures of vanadium(V) oxide and rutile were prepared and thermal analysis was carried out in nitrogen and oxygen. For samples containing 30% w/w V_2O_5 , two significant weight changes were observed, the first between 580 and 650° and the second between 750 and 950°. Although it had been observed that vanadium(V) oxide lost weight continuously at high temperatures, the rate increasing with temperature above 750°, samples containing rutile displayed a very much more sudden weight loss in the temperature region 750 to 950°. It was not possible to determine accurately the DTA traces for the vanadium(V) oxide—rutile system because, above 750°, the weight loss from V_2O_5 was an endothermic process. However, a slight endothermic peak was observed at ca. 900°.

The variation with mixture composition of the weight losses at 580–650° and 750–950° was investigated for samples heated in nitrogen and oxygen (Fig. 5). Between 580 and 650° and in both gases, the weight loss reached a maximum for mixtures containing ca. 5% w/w V_2O_5 . At higher temperatures, the weight loss also varied with composition, a maximum being observed for samples containing ca. 30% w/w V_2O_5 heated in nitrogen and for samples containing ca. 20% w/w V_2O_5 heated in oxygen. It was also found that the magnitude of the weight loss from a particular mixture was affected by the oxygen content of the atmosphere (up to 10% v/v) within the temperature range 750–950°. Oxygen had no effect on the weight loss from 580 to 650°.

Analysis by X-ray diffraction of vanadium(V) oxide–rutile mixtures, before and after these had been heated to 750 and 950° in nitrogen, revealed that no intermediate compound was present. The X-ray diffraction pattern of a mixture

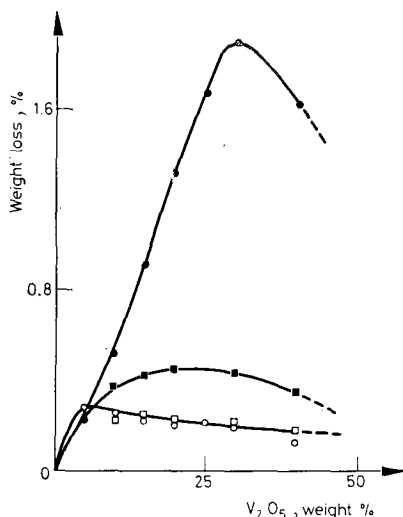


Fig. 5. The variation of weight loss with composition of vanadium(V) oxide – titanium(IV) oxide (rutile) mixtures. ○, samples heated to 580–650° in nitrogen; ●, samples heated to 750–950° in nitrogen; □, samples heated to 580–650° in oxygen; ■, samples heated to 750–950° in oxygen.

containing 30% w/w V_2O_5 , determined by means of the hot-stage apparatus, showed, however, that, between 550 and 600°, lines due to vanadium(V) oxide disappeared and, at 750°, other lines appeared which did not correspond to either V_2O_5 or rutile.

2. Vanadium(V) oxide – molybdenum(VI) oxide

The results of the thermal analysis of V_2O_5 – MoO_3 mixtures carried out in nitrogen and in oxygen have been described elsewhere [5]. As with the V_2O_5 – TiO_2 system, the magnitude of the weight loss varied with the composition of the oxide mixture and with the nature of the surrounding atmosphere. For example, the heating in nitrogen of vanadium(V) oxide–molybdenum(VI) oxide mixtures was characterised by a single weight loss (maximum weight loss ca. 1.1% for a mixture containing 70% w/w V_2O_5) between 580 and 720°. Similar measurements in oxygen revealed three distinct weight changes: a gradual weight loss (570–650°), a more sudden weight loss (650–660°) and a fairly rapid weight gain (660–670°). In oxygen, the maximum loss in weight (ca. 0.2%) was observed with a mixture containing 40% w/w V_2O_5 in the temperature range 650–660°.

At lower temperatures (570–650°), the maximum weight loss (ca. 0.2%) was observed with a mixture containing 90% w/w V_2O_5 .

The results of DTA for vanadium(V) oxide–molybdenum(VI) oxide mixtures containing 70, 50 and 30% w/w MoO_3 in both nitrogen and oxygen atmospheres are shown in Fig. 6. With all three mixtures, the DTA curves in oxygen were qualitatively very similar, the main feature being a sharp, double endotherm

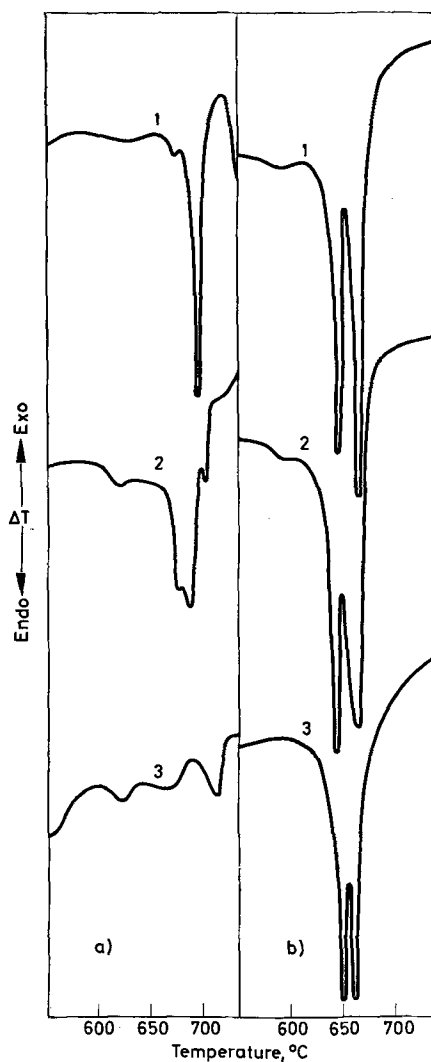


Fig. 6. Differential thermal analysis of vanadium(V) oxide–molybdenum(VI) oxide mixtures. (a) Behaviour in nitrogen; (b) Behaviour in oxygen. 1. 30% w/w V_2O_5 ; 2. 50% w/w V_2O_5 ; 3. 70% w/w V_2O_5 .

Table 2
DTA results for some V_2O_5 — MoO_3 mixtures

| Initial composition | Atmosphere | Appearance of DTA peaks | Extrapolated onset temperature, °C | Temperature interval for weight change, °C |
|-------------------------------|------------|---|------------------------------------|--|
| 30% w/w V_2O_5 — MoO_3 | N_2 | Broad endotherm | 592 | — |
| | | Sharp endotherm | 655 | — |
| | | Large endotherm | 692 | 692—709 |
| | | Endotherm | 727 | |
| | O_2 | Broad endotherm | 576 | 576—613 |
| | | Sharp, double endotherm | 642, 657 | 642—650 657—670 |
| 50% w/w V_2O_5 — MoO_3 | N_2 | Four endotherms: small, broad, sharp, double sharp | 600 | 672—702 |
| | | | 672, 672 | 705—715 |
| | | | 705 | |
| | | | | |
| | O_2 | Three endotherms | 582 | |
| | | | 633 | 633—653 |
| 614 | | | 614—676 | |
| 70% w/w V_2O_5 — MoO_3 | N_2 | Three small endotherms | 605 | 605—645 |
| | | | 600 | 600—692 |
| | | | 700 | 700—725 |
| | O_2 | Very sharp endothermic doublet | 648 | 648—659 |
| | | | 648 | 648—675 |
| | | | | |

which was observed between 650 and 675° (Fig. 6(b)). The DTA curves obtained by heating the mixtures in nitrogen were more complex (Fig. 6(a)). For example, with a mixture containing 30% w/w V_2O_5 , heating in nitrogen revealed a broad endotherm with an onset temperature at 592°. Superimposed on this is a smaller, sharp endotherm with an onset temperature at 655°. A very much more energetic process occurs as the temperature is raised to the onset temperature of 692°, the temperature interval for the reaction being 17°. Finally, after an exothermic process another endotherm can be observed, the onset temperature of which is 727°. The DTA results are summarised in Table 2.

Vanadium(V) oxide—molybdenum(VI) oxide mixtures were analysed by X-ray powder diffraction before and after being heated in nitrogen and oxygen. Mixtures heated to 600° in both gases were found to contain V_2O_5 and MoO_3 only. Further heating to 650° in oxygen did not alter the nature of the oxides. For a mixture containing 50% w/w V_2O_5 , heating in oxygen at 660 and 670° brought about the formation of the compound $Mo_6V_9O_{40}$. Similar results were obtained after the same mixture had been heated in nitrogen to 700°.

3. Vanadium(V) oxide–zirconium(IV) oxide

Mixtures of vanadium(V) oxide and zirconium(IV) oxide (as baddeleyite) were prepared and thermal analysis was carried out in both nitrogen and oxygen. As with the V_2O_5 -containing system previously described, weight loss from the samples was found to vary with mixture composition. The curves showed a maximum at 15% w/w V_2O_5 for the weight loss between 590 and 670°, and at 20% w/w V_2O_5 for the weight loss between 690 and 710°. In contrast to the V_2O_5 – TiO_2 and V_2O_5 – MoO_3 systems, the weight loss from a particular mixture was not affected by the presence of oxygen in the heating atmosphere. DTA of a mixture containing 15% w/w V_2O_5 showed two features, a very broad endotherm with an onset temperature at 574° and a very much sharper peak with an onset temperature at 676° and a temperature interval for the reaction of 29°.

X-ray examination of mixtures containing 15% w/w V_2O_5 and heated to 670 and 720° indicated that no compound formation had occurred.

4. Vanadium(V) oxide–zinc (II) oxide

The thermal behaviour of V_2O_5 – ZnO mixtures was not thoroughly investigated, since this system is not of interest from a catalytic point of view [5]. However, it was found that vanadium(V) oxide–zinc(II) oxide mixtures exhibited no weight changes below 750° in either nitrogen or oxygen. DTA traces of mixtures containing 70% w/w V_2O_5 showed two sharp endotherms, the first from 633 to 647° and the second from 655 to 668°.

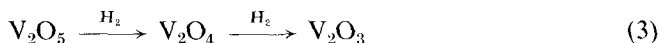
Discussion

Thermal studies of binary mixtures of vanadium(V) oxide and the three phase modifications of titanium(IV) oxide have shown that oxygen is evolved from the V_2O_5 at temperatures above 600°. Particularly significant is the fact that, for the three V_2O_5 – TiO_2 systems, 10–15 mole % V_2O_5 (ca. 25% w/w V_2O_5) represents the optimum concentration for evolution of oxygen and that this composition also coincides with the maximum catalytic activity of such mixtures [2]. In the case of V_2O_5 –brookite and V_2O_5 –anatase mixtures, oxygen evolution was accompanied by a gradual phase-transformation involving the titanium(IV) oxide. It was also found that, with samples containing less than 25% w/w V_2O_5 , the extents of oxygen evolution and of phase-transformation were both proportional to the concentration of vanadium(V) oxide present. Obviously V_2O_5 affected the transformation, oxygen being evolved as a direct result.

The thermal behaviour of titanium(IV) oxide has been investigated by various workers [12]. Despite the fact that the exothermic transformation of anatase to rutile at about 750° has been reported elsewhere [13, 14], in the present work no peaks were observed below 950° which could be attributed to the interconversion of anatase into rutile.

As regards the thermal behaviour of vanadium oxides, studies have been carried out mainly on mixtures containing vanadium in more than one oxidation state [15, 16]. With reference to the present work on vanadium(V) oxide–titanium(IV) oxide mixtures, assignment of specific processes to the recorded DTA traces is tentative. In Table 1, it is proposed that, for the vanadium(V) oxide–anatase system, the endothermic processes represent loss of oxygen from the V_2O_5 and the conversion of anatase into rutile followed by melting of the vanadium oxide. The fact that the onset temperature of the second endotherm varies is probably a reflection of the fact that the composition of the resulting vanadium oxide is not unique. For a vanadium(V) oxide–brookite mixture heated in nitrogen, the broad endotherm having an onset temperature at 623° may be assigned to the concurrent conversions of brookite into rutile and of V_2O_5 into V_2O_4 . The sharp endotherm at the higher temperature again represents the melting of “vanadium oxide”. In oxygen, three endotherms were observed with vanadium(V) oxide–brookite mixtures. In order of increasing onset temperature, it is suggested that these endotherms represent the brookite \rightarrow anatase phase-change (accompanied by loss of oxygen from the V_2O_5), the anatase \rightarrow rutile transformation (also with concurrent evolution of oxygen) and the melting of vanadium oxide. On account of the volatility of vanadium(V) oxide, it was not possible to determine accurately the DTA trace for V_2O_5 –rutile mixtures. The slight endothermic peak observed at ca. 900° may however be due to the formation of a $TiO_2 \cdot VO_x$ compound, since unidentifiable lines were observed during hot-stage X-ray diffraction studies of this system.

Finally, as regards the behaviour of vanadium(V) oxide–titanium(IV) oxide mixtures in hydrogen, the two-stage weight loss observed between 500 and 700° suggests the occurrence of the reactions:



For samples previously heated to 700° in nitrogen, the loss of weight in the presence of hydrogen was smaller than that from samples previously heated to 600° in both cases. The greatest weight loss was observed with mixtures containing 25% w/w V_2O_5 and this reflected the maximum production of a single reduced vanadium species (such as V^{4+}) at the higher temperature, as reported previously [2]. In the vanadium(V) oxide–titanium(IV) oxide mixtures, evidence has also been obtained for the incorporation of V^{4+} ions into the TiO_2 lattice during the phase-transformation [2]. The tendency of such ions, located within the rutile lattice, to be stabilised against re-oxidation on exposure to oxygen was confirmed by the finding that vanadium(V) oxide–titanium(IV) oxide mixtures containing 25% w/w V_2O_5 did not, after being heated, regain weight when heated in oxygen, although vanadium(III) oxide– and vanadium(IV) oxide–rutile mixtures did so.

As regards the correlation between the physicochemical and catalytic properties of the V–Ti–O system, it has been shown that 10–15 mole % V_2O_5 represents the optimum concentration for high-temperature solid-state reactions involving the components [2]. This composition was also found to coincide with the maxi-

imum catalytic activity of such mixtures for the oxidation of *o*-xylene. In the previous work [2], it was concluded that, at this composition, there is maximum contact between the oxide particles, whilst, at higher concentrations of vanadium(V) oxide, excess V_2O_5 particles do not make physical contact with those of TiO_2 . Indeed, structural interactions at the TiO_2/V_2O_5 interface may be responsible for the high-temperature solid-state reactions leading to V^{4+} ions stabilised within the rutile lattice. The latter species may then facilitate adsorption of *o*-xylene as a result of electron donation from the hydrocarbon to the V^{4+} ion to form what may be effectively termed a π -bonded complex.

Thermal studies of the V–Mo–O system have shown that, as with vanadium(V) oxide – titanium(IV) oxide mixtures, oxygen is evolved during heating. When samples are heated in nitrogen, a single weight loss is observed which has a maximum value for mixtures containing 25–30% w/w MoO_3 , whilst in oxygen more complex behaviour is observed, associated only in part with that of V_2O_5 . The evolution of oxygen from vanadium(V) oxide – molybdenum(VI) oxide mixtures has been observed by other workers [6, 8, 17] and the present results are substantially in agreement with their observations. Assignment of specific chemical events to the DTA peaks recorded in Table 2 is more difficult than with the V–Ti–O system. Pure molybdenum(VI) oxide did not lose weight until after it had melted (at 795°), when volatilisation was observed. Certain lower oxides of molybdenum, such as Mo_9O_{26} , Mo_8O_{23} and Mo_4O_{11} , appear to melt at about 700° [18], so that endotherms occurring in this temperature region are tentatively assigned to the melting of such oxides. Endotherms observed at temperatures below 700° cannot be identified, but they must be characteristic of the reduction of V_2O_5 to V_2O_4 and of the formation of compounds such as $Mo_6V_9O_{40}$. However, since the onset temperature of these processes is dependent on mixture composition and the nature of the surrounding atmosphere, further work is required before an unambiguous assignment can be made.

With vanadium(V) oxide – molybdenum(VI) oxide mixtures, the formation of an intermediate compound has been reported by other workers [6, 8, 17, 19] and Munch and Pierron [8] suggest that this is $Mo_6V_9O_{40}$. This compound is apparently converted to $Mo_4V_6O_{25}$ during the oxidation of hydrocarbons over vanadium(V) oxide – molybdenum(VI) oxide catalysts [8]. Although $Mo_6V_9O_{40}$ was readily identified by X-ray diffraction, in the present work no evidence was obtained for the presence of $Mo_4V_6O_{25}$.

It seems doubtful, therefore, whether the observed differences in thermal behaviour in nitrogen and oxygen can be explained in terms of the formation of two different intermediate compounds. Some indications as to the cause of the difference, may, however, be obtained from the observed weight losses and the identities of the resulting oxides.

From thermogravimetric data, it is possible to calculate the formula of the Mo–V oxide. If it is assumed that molybdenum(VI) oxide and vanadium(V) oxide react in the ratio $4 MoO_3 : 3V_2O_5$ [8] and that oxygen is derived from the vanadium(V) oxide only, a formula of $Mo_6V_9O_{39.6}$ is obtained for the oxide

remaining after being heated in nitrogen. A similar calculation shows that the oxide formed after being heated in oxygen at 660° is $\text{Mo}_6\text{V}_9\text{O}_{40.3}$. It is likely, therefore, that vanadium(V) oxide–molybdenum(VI) oxide mixtures containing 50% w/w V_2O_5 , when heated in nitrogen, form a compound closely related to $\text{Mo}_6\text{V}_9\text{O}_{40}$ but with a small proportion of oxygen anion vacancies. Similarly, the heating of such mixtures in oxygen probably brings about the formation of a similar compound containing a small excess of oxygen anions. Additionally, the formation of the latter compound might have been inhibited by oxygen and this would account for the observed slow reaction, at the end of which the reaction mixture contained both the constituent oxides and the intermediate compound, which then underwent a very rapid reaction. These compounds are not, however, thought to be of significance from the catalytic point of view.

Directly comparable with vanadium(V) oxide–titanium(IV) oxide mixtures is the V–Zr–O system. Mixtures of V_2O_5 and ZrO lost weight in the temperature range 590 – 710° , although they showed certain differences in behaviour from mixtures containing TiO_2 . Firstly, the weight loss for the zirconium(IV) oxide system occurred in two separate stages and, secondly, the magnitude of the weight loss was unaffected by the proportion of oxygen in the atmosphere in which the mixture was heated. Although the evolution of oxygen from vanadium(V) oxide–zirconium(IV) oxide mixtures has been reported by other workers [20, 21], no quantitative measurements appear to have been made nor has two-stage weight loss been reported. The results of Matkovich and Corbett [20] show some agreement with the present findings, but at the same time there are significant differences. For example, in the present work, it was shown that the two weight losses were both accompanied by endothermic peaks on the DTA trace. In contrast, Matkovich and Corbett [20] observed an endothermic peak at 660° (ascribed to the melting of V_2O_5) as well as an exothermic peak at 730° , believed to represent a reaction between vanadium(V) oxide and zirconium(IV) oxide, which is accompanied by the evolution of oxygen. The present investigation showed that oxygen evolution is complete at 710° and that no exothermic process occur in that temperature region. Experimentally, it was found that heating rates in excess of 5° min^{-1} tend to initiate the second weight loss before the completion of the first and, under these conditions, the DTA trace shows the first peak as a slight shoulder on the second, larger peak. Only at low heating rates ($< 5^\circ \text{ min}^{-1}$) were the two peaks well-defined. Although this may explain the single endothermic peak observed by Matkovich and Corbett [20], who used a heating rate of 10^0 min^{-1} for DTA, the observation of an exothermic peak cannot be similarly explained. Finally, although it has been suggested [20] that the product of the solid-state reaction was a compound of the form $\text{ZrO}_2 \cdot n\text{V}_2\text{O}_x$, where $x = 4$ or 5 , no intermediate compound was formed when vanadium(V) oxide–zirconium(IV) oxide mixtures were heated to 670 or 720° . Zirconium(IV) oxide is a promoter of vanadium(V) oxide for the catalytic oxidation of *o*-xylene and the preferred catalyst composition is very close to that for maximum oxygen evolution (5–10 mole % V_2O_5).

Vanadium(V) oxide, promoted by very small quantities ($< 1\%$ w/w) of zinc(II) oxide, is claimed to be a good catalyst [22] for the oxidation of *o*-xylene. However, V_2O_5-ZnO catalysts of composition similar to those of useful $V_2O_5-TiO_2$ catalysts were neither particularly active nor selective. According to Galy and Hagenmuller [23] and Clark and Pick [9], zinc(II) oxide undergoes reaction with vanadium(V) oxide at temperatures around 600° , suggesting that an optimum composition exists in this system for compound formation.

Although high-temperature reactions and compound formation were observed in the present system, no weight changes were observed over the temperature range within which $V_2O_5-TiO_2$ and $V_2O_5-ZrO_2$ mixtures lost weight. An investigation of the catalytic properties of the V-Zn-O system did not reveal any enhancement of the catalytic activity of vanadium(V) oxide by zinc(II) oxide. Indeed the activity towards *o*-xylene oxidation increased linearly with V_2O_5 concentration.

In conclusion, it appears that a useful indication of the catalytic activity of binary oxide mixtures containing vanadium(V) oxide is their thermal behaviour and, in particular, their thermogravimetric properties. The occurrence of high-temperature solid-state reactions involving the reduction of V_2O_5 to V_2O_4 is characterised by the evolution of oxygen from such systems and the optimum mixture composition for oxygen evolution has been shown to coincide with that for maximum catalytic activity. The literature suggests that the reduction of V_2O_5 to V_2O_4 in the presence of even small amounts of oxygen is at best extremely slow at temperatures below 650° [15, 24-28]. However the present work, in conjunction with previous results [2, 5], has shown that certain transition metal oxides can accelerate this conversion. Such acceleration may be caused by structural interactions at the interface of the oxides [2] and has important implications from the catalytic point of view.

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RÉSUMÉ — L'étude du comportement thermique de mélanges d'oxydes binaires contenant de l'oxyde de vanadium(V) ($V_2O_5-TiO_2$, $V_2O_5-MoO_3$, $V_2O_5-ZrO_2$ et V_2O_5-ZnO) a montré que le dégagement de gaz oxygène à température relativement faible est caractéristique des systèmes qui sont des catalyseurs actifs de l'oxydation des hydrocarbures. Avec les mélanges V_2O_5-ZnO , on n'a pas observé de variations pondérales dans les mêmes conditions et, en accord avec l'observation faite, l'oxyde de zinc(II) n'augmente pas l'activité catalytique de l'oxyde de vanadium(V). Dans les systèmes contenant V_2O_5 , le dégagement d'oxygène a lieu au cours de la réduction de V_2O_5 en V_2O_4 . Cette réaction est accélérée en présence de certains oxydes métalliques. Le phénomène d'accélération peut être dû à des interactions structurales à l'interface des oxydes. Dans les systèmes étudiés, la formation de composés comme $Mo_6V_9O_{40}$ est considérée de peu d'importance du point de vue catalytique.

ZUSAMMENFASSUNG — Die Untersuchung des thermischen Verhaltens vanadium(V)-oxidhaltiger binärer Mischungen ($V_2O_5-TiO_2$, $V_2O_5-MoO_3$, $V_2O_5-ZrO_2$ und V_2O_5-ZnO) ergab, daß die Entwicklung gasförmigen Sauerstoffs bei niedrigen Temperaturen für jene Systeme, welche effektive Katalysatoren der Oxidierung von Kohlenwasserstoffen sind, charakteristisch ist. Keine Gewichtsänderungen wurden bei Mischungen von V_2O_5-ZnO unter diesen Bedingungen beobachtet und dementsprechend fördert Zink(II) Oxid die katalytische Aktivität von Vanadium(V) Oxid nicht. In V_2O_5 -haltigen Systemen erfolgt die Sauerstoffentwicklung während der Reduktion von V_2O_5 zu V_2O_4 . Dieser Vorgang wird durch die Anwesenheit gewisser Metalloxide beschleunigt und kann durch strukturelle Wechselwirkungen an der Grenzfläche der Oxide gedeutet werden. Bei den untersuchten Systemen wird die Bildung von Verbindungen wie $Mo_6V_9O_{40}$ vom Gesichtspunkt der Katalyse als wenig bedeutend betrachtet.

Резюме — Изучение термического поведения двойных окисных смесей, содержащих пятиокись ванадия (V_2O_5 — TiO_2 , V_2O_5 — MoO_3 , V_2O_5 — ZrO_2 и V_2O_5 — ZnO), показало, что выделение газообразного кислорода при достаточно низких температурах является характерным для тех систем, которые являются эффективными катализаторами окисления углеводородов. В случае смесей V_2O_5 — ZnO не наблюдали изменения веса в аналогичных условиях, что согласуется с тем, что окись цинка(II) не усиливает каталитическую активность пятиокиси ванадия. В системах, содержащих пятиокись ванадия, выделение кислорода происходит во время восстановления V_2O_5 до V_2O_4 . Этот процесс ускоряется в присутствии определенных окислов металлов и такое ускорение может быть обусловлено структурными взаимодействиями на поверхности раздела окислов. С каталитической точки зрения образование таких соединений как $Mo_6V_9O_{40}$ в изученных системах, имеет малое значение.