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THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE SUPPORTED ON Al_2O_3

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ABSTRACT

The thermal decomposition of ammonium metavanadate supported on aluminium oxide was investigated using DTA, TG and X-ray diffraction techniques.

The results obtained revealed that ammonium vanadate decomposed at 225–250°C giving an intermediate compound ($(NH_4)_2V_6O_{16}$) which decomposed readily at 335–360°C producing V_2O_5. Alumina was found to ehance the formation of the intermediate compound and retard its decomposition. Some of the V^{5+} ions of V_2O_5 lattice seemed to be reduced into V^{4+} and V^{3+} ions by heating in air at 450°C in the presence of Al_2O_3. Such a reaction was attributed to dissolution of some Al^{3+} ions in the V_2O_5 lattice via location in interstitial positions and/or in cationic vacancies. Al_2O_3 was found to interact with V_2O_5 at 650°C giving well-crystalline $AlVO_4$ which decomposed at about 750°C forming well-crystalline δ-Al_2O_3 and V_2O_5. Pure Al_2O_3, heated in air at 1000°C, existed in the form of the κ-phase which, on mixing with V_2O_5 (0.5 V_2O_5:1 Al_2O_3) and heating in air at 1000°C, was converted entirely to the well-crystalline α-Al_2O_3 phase.

INTRODUCTION

The thermal decomposition of ammonium metavanadate made the object of several investigations [1–9]. The decomposition process takes place according to different mechanisms depending, mainly, upon the atmosphere in contact with the solid. In an N_2 atmosphere or under a reduced pressure of 10^{-6} Torr, NH_4VO_3 decomposes readily giving V_3O_7 [2,4,6] while in an O_2 atmosphere V_2O_5 represents the thermal product of the solid metavanadate [1,3,7–9]. Indeed, the thermal decomposition in O_2, or in dry air, proceeds through the formation of an intermediate compound ($(NH_4)_2V_6O_{16}$) [4,5].

The effect of a support on the thermal decomposition of ammonium metavanadate, to our knowledge, has not yet been investigated. The present work reports a study on the thermal decomposition of ammonium metavanadate supported on γ-Al_2O_3. The techniques employed were DTA, TG, DTG and X-ray diffraction.

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EXPERIMENTAL

Materials

Gamma-alumina, precalcined in air at 500°C, was impregnated with different proportions of ammonium metavanadate dissolved in dilute NH_4OH using a pore-filling method. The composition of the impregnated solids was 0.1 NH_4VO_3:Al_2O_3, 0.4 NH_4VO_3:1 Al_2O_3 and 1.0 NH_4VO_3:1.0 Al_2O_3, and the solids were dried at 110°C to constant weight.

Techniques

Differential thermal analysis of various impregnated solids was carried out using a Netzsch-Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10°C min^{-1}. A 200-mg sample of each solid specimen was employed in each case.

An X-ray investigation of the thermal products of pure ammonium metavanadate and the metavanadate supported on aluminium oxide was performed with a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation, $\lambda = 1.5405$ Å at 40 kV and 25 mA with a scanning speed of 2° in 2θ min^{-1}.

RESULTS AND DISCUSSION

Thermal decomposition of ammonium metavanadate supported on Al_2O_3 (0.1 NH_4VO_3:1 Al_2O_3)

Figure 1 represents the DTA, TG and DTG curves of 0.1 NH_4VO_3:1 Al_2O_3. Three endothermic peaks are observed, the first is very strong, the second is weak and rapid and the third is sharp and relatively strong. The maxima of these peaks are located at 130, 355 and 655°C, respectively. The first peak, which was followed by a 5.3% loss in weight, indicated desorption of physisorbed water, retained in the Al_2O_3 solid. The second peak was accompanied by a loss in weight of 5.3% and corresponded to the decomposition of NH_4VO_3. The peak at 655°C was not followed by any change in weight and may characterize a phase transformation of Al_2O_3 solid or a solid–solid interaction between vanadium and aluminium oxides. The identification of such a change will be made by X-ray diffraction, in the next part of the present investigation. The total recorded weight loss, from room temperature to 800°C, was 11.7%.

0.4 NH_4VO_3:1 Al_2O_3

Figure 2 represents the DTA, TG and DTG curves of 0.4 NH_4VO_3:1 Al_2O_3. Four endothermic peaks are found: the first is very strong; the

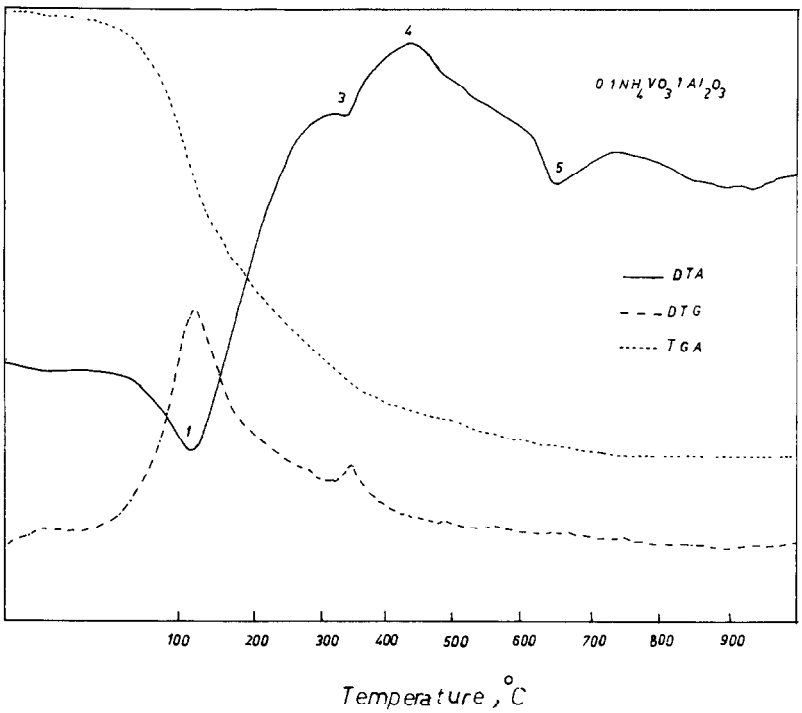

Fig. 1. DTA, TG and DTG curves of 0.1 NH_4VO_3:1 Al_2O_3.

second and the third are weak and rapid; the fourth is strong. The maxima of these peaks are located at 130, 225, 360 and 660°C, respectively. A possible exothermic peak at 420°C can be also observed from Fig. 2. The weight loss corresponding to the four endothermic peaks attains 5.7, 3.6, 2.3 and 0.0%, respectively. The exothermic peak was followed by 0.8% weight loss and the total weight loss, up to 800°C, was 13.3%. The second and third endothermic peaks at 225 and 360°C indicated the decomposition of NH_4VO_3 to an intermediate compound which underwent thermal decomposition giving V_2O_5. This speculation will be confirmed by the X-ray diffraction study presented in the next part of this work. The last endothermic peak at 660°C, which was not followed by any change in weight, indicated a phase transformation or a solid–solid interaction between aluminium and vanadium oxides.

1.0 NH_4VO_3:1 Al_2O_3

Figure 3 represents the DTA, TG and DTG curves of ammonium meta-vanadate and Al_2O_3 in equimolar ratio. Four endothermic peaks are observed, the first two and the last one are sharp and strong while the third is weak and rapid. The maxima of these peaks are located at 130, 250, 235 and 665°C, respectively. An exothermic peak at 430°C, similar to that found in

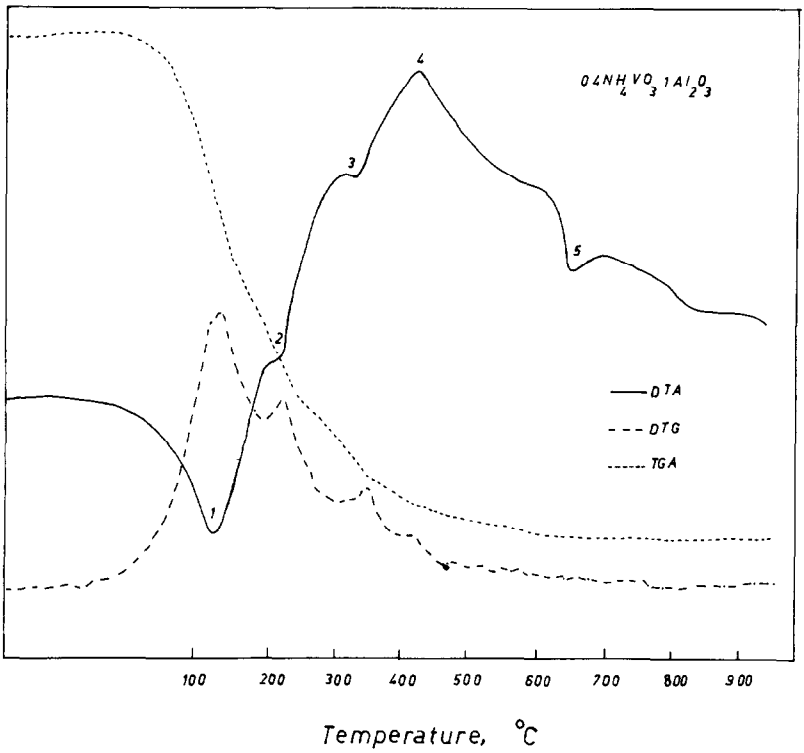

Fig. 2. DTA, TG and DTG curves of 0.4 NH_4VO_3:1 Al_2O_3.

the case of 0.4 NH_4VO_3:1 Al_2O_3, is also observed. However, this peak was accompanied by a weight loss of 1.5%. The weight losses corresponding to the four endothermic peaks are 4.1, 6.2, 3.8 and 0.0%, respectively. The total weight loss, up to 800°C, was 15%. The second and third peaks indicated the decomposition of ammonium vanadate to an unstable intermediate compound which readily decomposed producing V_2O_5.

The comparison between Figs. 1–3 reveals that ammonium metavanadate at the smallest concentration, 0.2 NH_4VO_3:1 Al_2O_3, decomposed in one step and in two distinct steps in the case of the other concentrations. The percentage weight loss corresponding to the decomposition of ammonium metavanadate increased on increasing its concentration. Furthermore, the area of the last endothermic peak, not accompanied by any weight loss, also increases on increasing the extent of ammonium metavanadate. This indicates that the last endothermic peak (peak 5) is more likely to be related to a solid–solid interaction between V_2O_5 and Al_2O_3.

The analysis of the data of thermal behaviour of different solids indicates that the weight loss corresponding to the decomposition of ammonium vanadate in different specimens attained 5.3, 5.9 and 10% for the solids containing 0.1, 0.4 and 1.0 mol NH_4VO_3/mol Al_2O_3, respectively. Further-

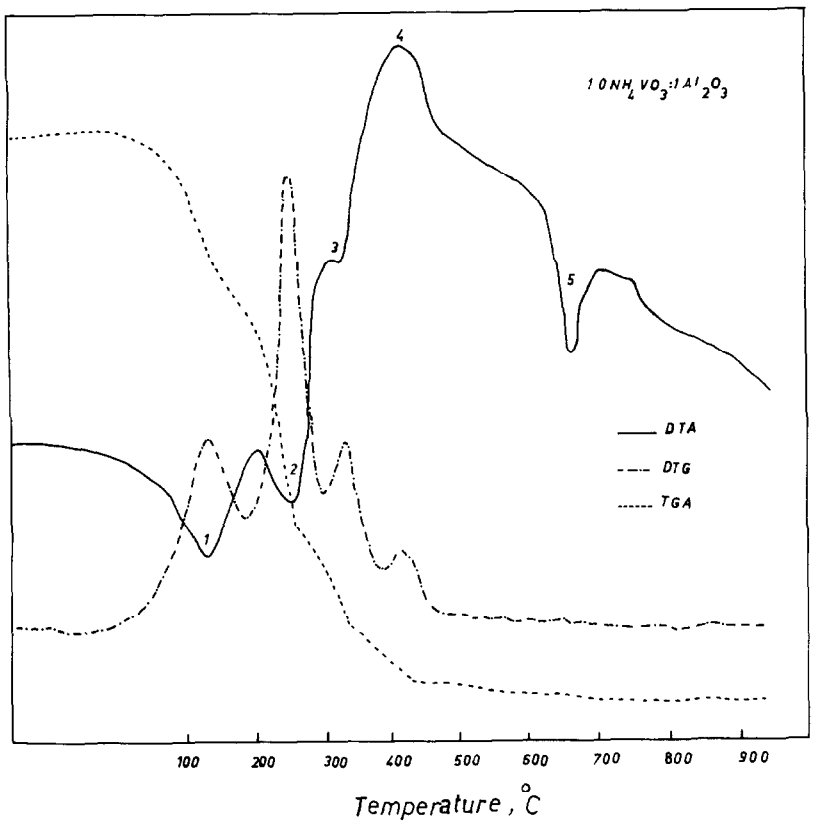

Fig. 3. DTA, TG and DTG curves of 1 NH_4VO_3:1 Al_2O_3.

more, the decomposition of ammonium metavanadate occurred in two distinct steps (except in the solid containing 0.1 NH_4VO_3). The first step is probably related to the formation of an intermediate compound while the second corresponded to its decomposition to produce V_2O_5. The maximum of the endothermic peak corresponding to the formation of the intermediate compound increased from 225 to 250°C on increasing the vanadate content from 0.4 to 1.0 mol/mol Al_2O_3. In contrast, the maximum related to the decomposition of the intermediate compound decreased from 360 to 335°C on increasing the vanadate content from 0.4 to 1.0 mol. These results indicate that the Al_2O_3 support enhanced the formation of the intermediate compound and retarded its decomposition.

Adopting the mechanism of the thermal decomposition of NH_4VO_3 [5,6] via the formation of $(NH_4)_2V_6O_{16}$ as an intermediate compound according to

$$6\ NH_4VO_3 \xrightarrow[Al_2O_3]{225-250°C} (NH_4)_2V_6O_{16} + 4\ NH_3 + 2\ H_2O \quad (1)$$

$$(NH_4)_2V_6O_{16} \xrightarrow[Al_2O_3]{335-360°C} 3\ V_2O_5 + 2\ NH_3 + H_2O \quad (2)$$

The weight losses corresponding to reactions (1) and (2) are 14.82 and 8.70%, respectively. The relative weight loss corresponding to reaction (1) is equivalent to 63% and that relative to reaction (2) is 37%. The observed relative weight loss for the thermal decomposition of NH_4VO_3 supported on Al_2O_3 attained 61:39% for the solid containing 0.4 mol NH_4VO_3 and 62:38% for Al_2O_3 treated with ammonium vanadate in equimolar ratio. The concordance between the theoretical and the observed data for the weight loss occurring during the thermal decomposition of ammonium metavanadate according to the mechanism represented by reactions (1) and (2) could be taken as evidence for the validity of such a mechanism in the present case.

X-ray investigation of the thermal products of various solids

Pure ammonium metavanadate

Different specimens of ammonium metavanadate were subjected to heating in air for 5 h at 300, 400, 500 and 600°C. The diffraction lines of the V_2O_5 phase were only detected in the X-ray diffraction patterns of different solids. However, the intensity of the diffraction lines was found to increase on increasing the calcination temperature from 300 to 400°C.

Pure aluminium oxide

Various samples of Al_2O_3, employed in the present work, were heated in air at various temperatures between 500 and 1000°C. The X-ray investigation revealed that Al_2O_3 heated at 500°C was poorly crystalline γ-alumina and its degree of crystallinity increased on increasing the calcination temperature to 900°C. Al_2O_3 heated at 1000°C existed in the form of κ-alumina [10].

Aluminium oxide treated with different proportions of NH_4VO_3

Different specimens of Al_2O_3, preheated at 500°C, were impregnated with various proportions of ammonium metavanadate and the solids produced were heated in air for 5 h at 500, 650, 750 and 1000°C. The X-ray investigation of these solids showed that all the solids heated at 500°C, except that treated with 1 mol NH_4VO_3/mol Al_2O_3, were composed of well-crystalline V_2O_5 phase and poorly crystalline γ-alumina. These results indicated the absence of a solid–solid interaction between Al_2O_3 and V_2O_5 at 500°C, giving new compound(s). Possible interaction between these two oxides could proceed at temperatures above 500°C. Figure 4 represents the X-ray diffraction patterns of the thermal products of Al_2O_3 treated with an equimolar ratio of NH_4VO_3. It is observed from Fig. 4 that, in the case of the solid heated at 500°C, all the characteristic diffraction lines of V_2O_5 together with few lines of δ-Al_2O_3 [10] of small intensity persisted in the diffraction patterns. It can be concluded that, similar to the case of the Al_2O_3 specimens treated with smaller amounts of NH_4VO_3, alumina could

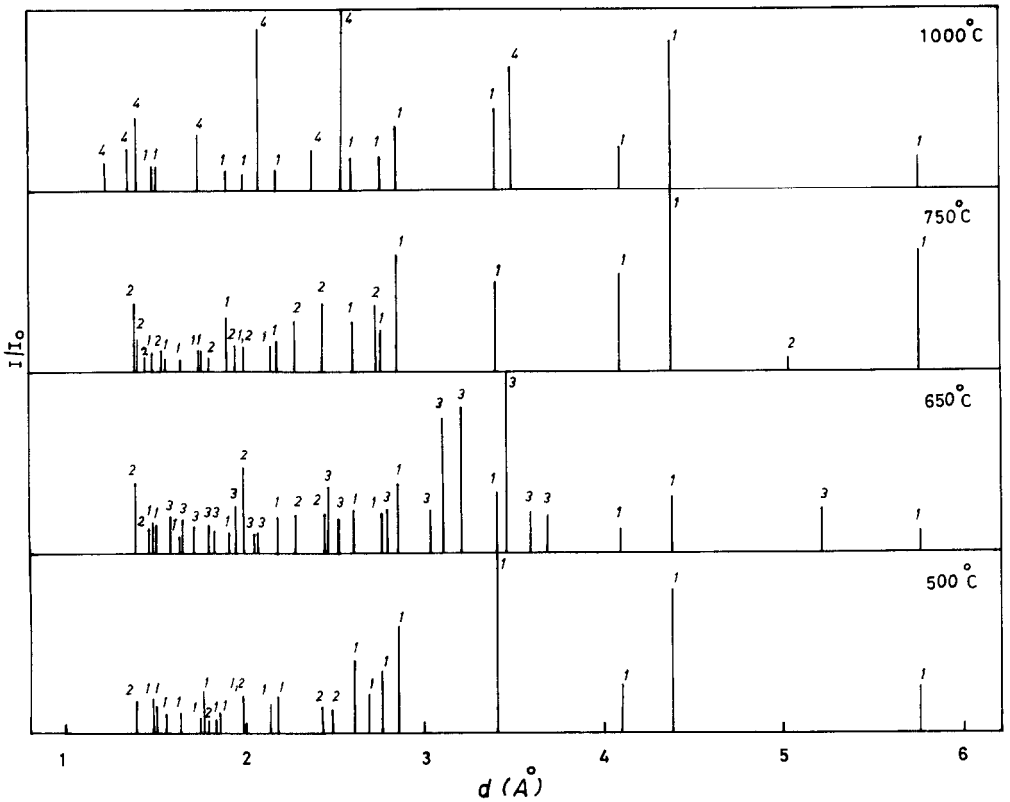

Fig. 4. X-ray diffraction patterns of the thermal products of 1 NH_4VO_3:1 Al_2O_3. (1) V_2O_5; (2) δ-Al_2O_3; (3) $AlVO_4$; (4) α-Al_2O_3.

not interact with V_2O_5 at 500°C to produce a new phase. However, γ-alumina was converted to δ-alumina in the presence of V_2O_5 (0.5 mol/mol Al_2O_3). Increasing the calcination temperature of the solid of composition 0.5 V_2O_5:1 Al_2O_3 to 650°C led to the formation of well-crystalline aluminium vanadate, $AlVO_4$ [10] (cf. Fig. 4) together with a small portion of unreacted V_2O_5 and δ-alumina. On this basis, the strong endothermic peak at 665°C observed in the DTA curves of various solids (peak 5, Figs. 1–3) indicated the solid–solid interaction between Al_2O_3 and V_2O_5 giving $AlVO_4$. This reaction, which proceeds according to

$$Al_2O_3 + V_2O_5 \overset{650°C}{\rightarrow} 2AlVO_4 \qquad (3)$$

is, in fact, not accompanied by any weight loss of the reacting species. The thermal treatment of the solid at 750°C caused the complete decomposition of aluminium vanadate into well-crystalline δ-alumina and V_2O_5 phases (cf. Fig. 4). The fact that the thermal decomposition of $AlVO_4$ has not been detected in the DTA curves of various solids (Figs. 1–3) indicated that such

a process occurred very slowly. Increasing the calcination temperature of the mixed oxide sample to 1000°C effected a phase transformation of δ-alumina to α-alumina and decreased the crystallinity of the V_2O_5 phase. These results, clearly indicate a mutual effect between the Al_2O_3 and V_2O_5 phases. The complete phase transformation of δ-alumina to α-alumina has been induced by V_2O_5 which lost some of its crystallinity.

The X-ray diffraction patterns, not presented here, of the solid of composition 0.2 V_2O_5:1 Al_2O_3 and heated in air at 1000°C revealed the presence of a mixture of δ- and α-aluminas together with well-crystalline V_2O_5. These results show that increasing the amount of V_2O_5 favoured the phase transformation process. It is well known that α-alumina can be produced by heating pure Al_2O_3 in air at temperatures above 1200°C [12–14]. The transformation of Al_2O_3 into α-alumina at 1000°C by treating with V_2O_5 pointed to the role of this oxide in enhancing or catalyzing such a phase transformation which depended on the molar ratio of the reacting oxides. It has been shown by MacKenzie and Hossini [15] that the thermal transformation of γ-Al_2O_3 to α-Al_2O_3 was effectively enhanced by an external d.c. electric field. α-Al_2O_3 was formed in the region of the positive electrode. This behaviour was thought to be due to the electric withdrawal of protons from the anode region and their migration to the cathode, where they stabilized the defect spinel structure of γ-Al_2O_3. The fact that the phase transformation of δ-alumina to α-alumina, occurring at 1000°C, has not been detected in the DTA curve of various solids, indicated that such a process took place with a relatively low rate.

The results of the thermal behaviour and X-ray diffraction studies of different solids showed that NH_4VO_3 supported on Al_2O_3 underwent thermal decomposition by heating in air giving V_2O_5 via the formation of an unstable intermediate compound. The formed oxides interacted in the solid state at 650°C giving $AlVO_4$. Below such a temperature some kind of a solid solution, not easily detected by a simple X-ray diffraction analysis, might exist between Al_2O_3 and V_2O_5. The ionic radii of Al^{3+} and V^{5+} ions are 0.50 and 0.59 Å, respectively [11]. Some of the Al^{3+} ions could be dissolved in the V_2O_5 lattice. Such a process might proceed according to: location in interstitial positions and/or in cationic vacancies; by substituting some of the pentavalent vanadium ions of the V_2O_5 lattice. These processes can be simplified, adopting Kröger's notions [16], as follows

$$Al_2O_4 + 3\,V^{5+} \rightarrow 2\,Al\boxed{\triangle} + 3\,V^{3+} + 3/2\,O_2(g) \quad (4)$$

$$Al_2O_3 + 6\,V^{5+} \rightarrow 2\,Al\boxed{\triangle} + 6\,V^{4+} + 3/2\,O_2(g) \quad (5)$$

$$Al_2O_3 + 2\,V^{3+} + O_2(g) \rightarrow 2\,Al(V^{5+}) + 2\,V^{5+} \quad (6)$$

$Al\boxed{\triangle}$ represents an aluminium ion located in an interstitial position or in a cationic vacancy, and $Al(V^{5+})$ a trivalent aluminium ion located in the position of host V^{5+} cations present in the V_2O_5 lattice. Reactions (4) and (5)

are accompanied by the transformation of some V^{5+} ions into V^{3+} and V^{4+} ions with the departure of a corresponding amount of O_2 from the V_2O_5 lattice. In other words, reactions (4) and (5) cause a weight loss of V_2O_5. In contrast, reaction (6) effects a gain in weight of V_2O_5 due to fixation of some of atmospheric oxygen into the solid with the subsequent transformation of trivalent vanadium ions into V^{5+} ions. Such a reaction requires the presence of V^{3+} ions in the V_2O_5 lattice [17]. This reaction cannot account for the experimental results obtained, simply because a weight loss has been detected in DTG and DTA curves of different solids (cf. the exothermic peak at 430°C, Figs. 1–3). It can be concluded that a portion of Al_2O_3 has been dissolved in the V_2O_5 lattice at temperatures around 430°C via location in interstitial positions and/or in cationic vacancies leading to the transformation of some V^{5+} ions to V^{3+} and/or V^{4+} ions. The solid solution thus formed underwent a chemical transformation by heating at 650°C giving $AlVO_4$.

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