

TEMPERATURE-PROGRAMMED DECOMPOSITIONS OF NH_4VO_3 AND $\text{NH}_4\text{VO}_3\text{-TiO}_2$ INVESTIGATED BY MASS-SPECTROMETRY AND DTA METHODS

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(Received July 27, 1978)

The thermal decompositions of NH_4VO_3 and $\text{NH}_4\text{VO}_3\text{-TiO}_2$ mixtures were investigated by mass-spectrometry and DTA. Three stages of decomposition were distinguished, in which the contribution of redox-type reactions increased successively. The bulk of the decomposition was independent of the nature of the atmosphere; only the third stage displayed a variation. In vacuo and in argon there was continuous reduction of the vanadium oxide system, but in air its reoxidation took place.

$\text{V}_2\text{O}_5\text{-TiO}_2$ catalysts are frequently used in the catalytic oxidation of *o*-xylene to phthalic anhydride, and the best selectivity appears at low V_2O_5 contents [1]. The role of TiO_2 was ascribed by Tarama *et al.* [2] to the weakening of the $\text{V}=\text{O}$ bond in vanadia. Blanchard and Louquet [3] observed a correlation between the activation energy of the $\text{O}^{16}/\text{O}^{18}$ exchange and the catalytic selectivity. However, Cole *et al.* [4] suggested that the mechanism of promotion involved only the efficient dispersal of V_2O_5 on the surface of the TiO_2 .

$\text{V}_2\text{O}_5\text{-TiO}_2$ catalysts are reduced by a reaction mixture of *o*-xylene and oxygen. Yabrov *et al.* [5] observed dissolution of V^{4+} ions in the rutile phase; also, V^{3+} ions were postulated. Lately, Grzybowska *et al.* [6] confirmed this by X-ray and chemical analysis, and noticed that a solid solution is not formed in anatase. Nonetheless, according to Courtine *et al.* [7], the reduction of V_2O_5 supported on anatase occurs at 400° , i.e. distinctly below the point of phase-transition of anatase into rutile. The reduction caused the formation of V_6O_{13} and Courtine postulated a stabilizing influence of anatase on this oxide phase. The necessity of considering the lower oxide of vanadium in the course of the catalytic oxidizing processes was the subject of a separate paper [8].

It seemed worthwhile in relation to the literature data to undertake a study of the thermal decompositions of ammonium metavanadate (AMV)– TiO_2 mixtures, especially since in an earlier work [9] the participation of redox reactions during the decomposition of AMV was described. Observations were made by the application of continuous mass-spectrometric analysis of the gaseous products of AMV decomposition. The lack of analogous measurements was the reason why, in the earlier proposed MVA decomposition models based mainly on TG, DTA and X-ray analysis, the redox reactions were either completely disregarded or were attributed by the authors to the reducing influence of the atmosphere [10, 11].

The measurements in [9] were carried out in vacuo. For this reason, in the present paper vacuum mass-analysis has been connected with differential thermal analysis (DTA), which can be carried out in argon and air at atmospheric pressure. Thus, the limitation that redox reactions take place only in vacuum conditions has been eliminated.

Experimental

Measurements were carried out with the following samples:

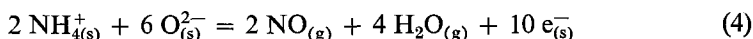
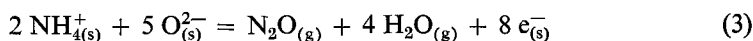
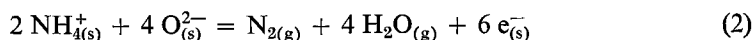
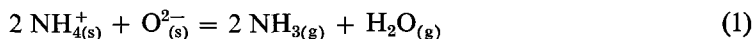
- I – pure AMV (Merck)
- II – mixture of I (20%) with TiO₂ (anatase) (Montecatini)
- III – pure AMV (POCh)
- IV – mixture of III (20%) with the same TiO₂.

Samples weighing about 20 mg were decomposed in vacuo with continuous rapid removal of the gaseous products and at a constant heating rate of about 1.3 deg/min. The gas stream flowed from the reactor into an ultrahigh vacuum system through a mass-spectrometer head. The details were presented in [9].

The DTA measurements were performed with an ATD M5 (Setaram) at the following parameters: weight of samples: 20 mg, flow velocity of gas: 20 ml/min, and heating rate: 1.5 deg/min. α -Al₂O₃ was used as reference material.

Results and discussion

Similarly as in the previous work, three consecutive stages were observed in the course of the temperature-programmed decomposition of AMV in vacuo. Besides water and ammonia, N₂, N₂O and NO were also detected among the gaseous products. This indicated that the total process consisted of four partial reactions:



They may be used to calculate the degree of decomposition, i.e. the conversion of an oxy-salt into an oxide as a percentage of the ammonium cations removed from the solid. They also allow the calculation of the deficit of oxygen in the decomposition product in relation to the strictly stoichiometric V₂O₅.

The electrons e⁻ indicated in the above equations are localized at the vanadium (V) atoms, causing their reduction. The problem as to which oxidation number of the V atoms is reached is still open. Dyrek, investigating partially, reduced

V_2O_5 , showed by an EPR method combined with chemical analysis that both V^{4+} and V^{3+} ions were present [12].

Starting from the values of partial pressures registered by mass-spectrometer, the relative velocities of reactions (1)–(4) were obtained and then, by integration,

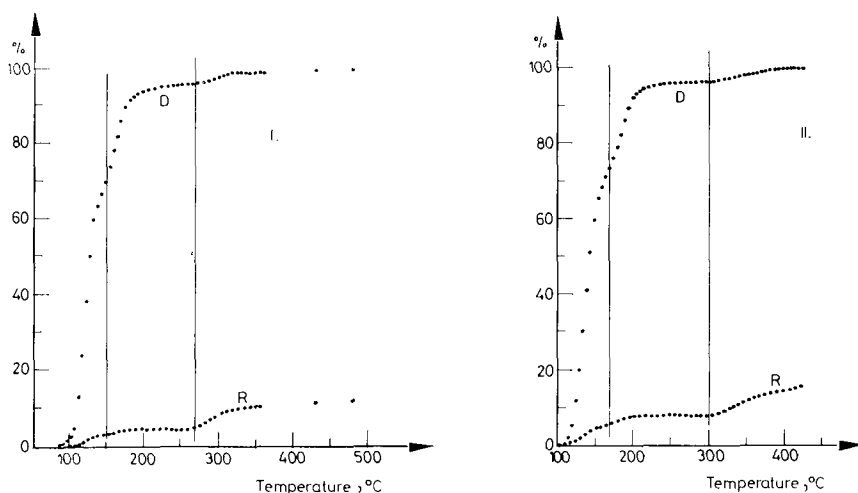


Fig. 1. D — Degree of decomposition expressed as a percent of the NH_4^+ ions removed. R — Reduction degree of the formed V_2O_{5-x} oxide system expressed as $100 \times$ value. I — Merck preparation of AMV; II — Merck preparation of AMV + TiO_2

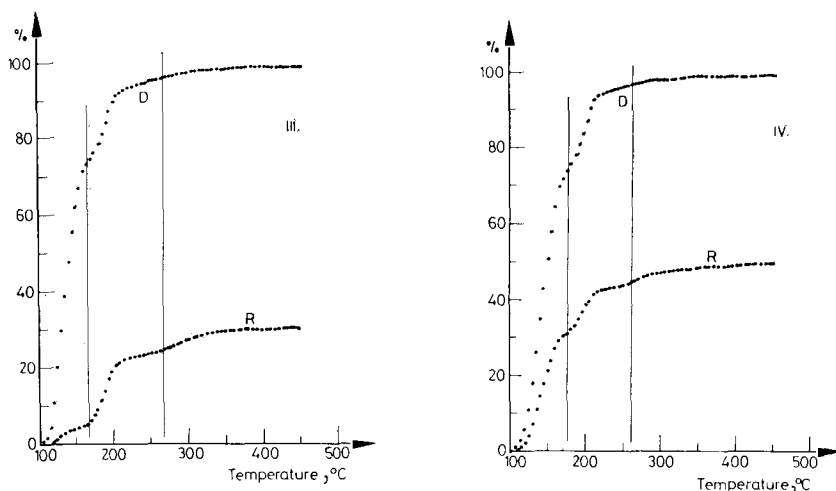


Fig. 2. D — Degree of decomposition expressed as a percent of the NH_4^+ ions removed. R — Reduction degree of the formed V_2O_{5-x} oxide system expressed as $100 \times$ value. III — POCh preparation of AMV; IV — POCh preparation of AMV + TiO_2

the average composition of the remaining solid was computed [9]. The present results are shown in Figs 1 and 2, as plots of the conversion and reduction degree versus temperature during the linear temperature-programmed decomposition of AMV.

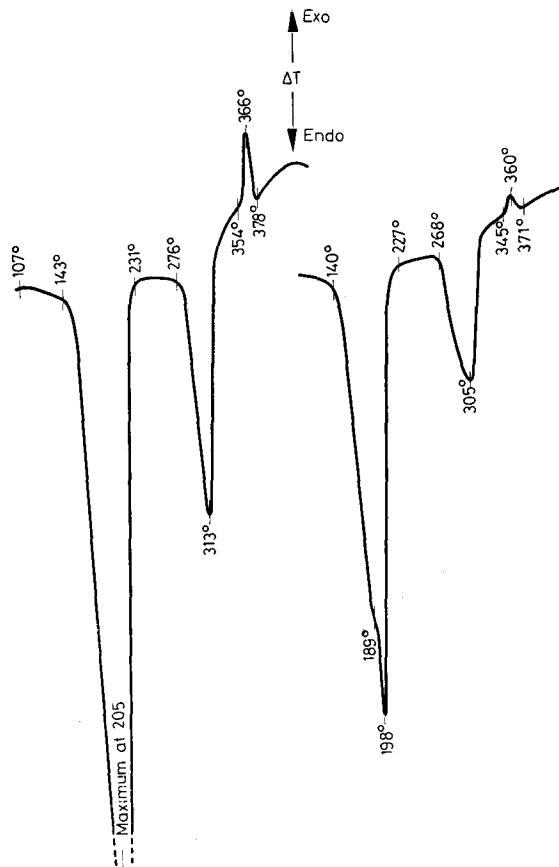


Fig. 3. DTA curves in argon stream for: I — Merck preparation of AMV; II — Merck preparation of AMV + TiO_2

In all samples, both in [9] and in the present study, three stages of decomposition were observed. The majority of the NH_4^+ ions were removed in the first stage (70–80%), but reduction took place mainly in the later stages, especially in the third one. Among the tested preparations of AMV, the most easily reduced is that from POCh, and the least that from Reachim. Most probably these various properties resulted from textural differences in the AMV preparations.

It is interesting to observe that the composition of the solid residue after the first stage of AMV decomposition was always within the range of existence of

vanadium-ammonium bronzes. Deschanvres *et al.* [13] studied the formation of such bronzes. They reported transformation of ammonium hexavanadate into a bronze-type compound with N_2 evolution, and observed the thermal decomposition of this bronze into monoclinic VO_2 with N_2 and H_2O evolution. It may be added that monoclinic VO_2 exists only below 70° . At higher temperatures the rutile-type lattice is stable. V_6O_{13} forms a monoclinic lattice in the whole range of temperature up to 700° [14].

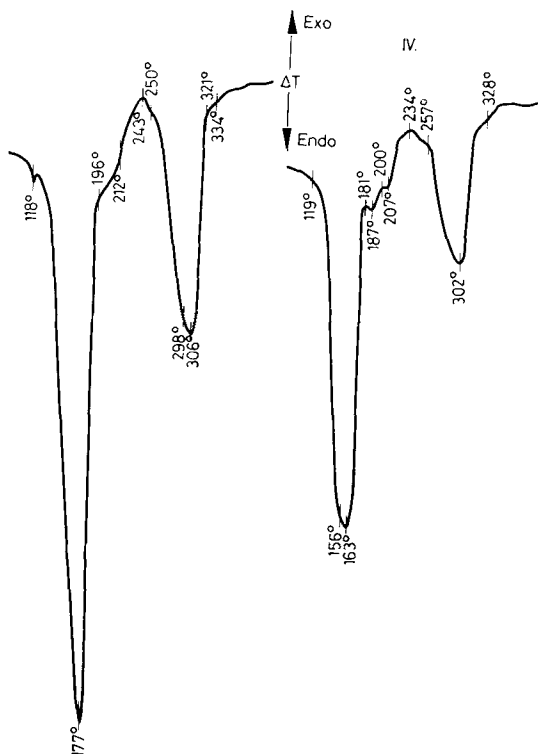


Fig. 4. DTA curves in argon stream for: III — POCh preparation of AMV; IV — POCh preparation of AMV + TiO_2

Comparing plots I with II (Fig. 1) and III with IV (Fig. 2), one may see that TiO_2 increases slightly the reduction degrees of the solid residue. The presence of titania, as was mentioned earlier [2, 5–7], increases the reducibility of the vanadia catalysts in the course of the catalytic oxidation of, for example, *o*-xylene. The analogous influence, an increasing of the reduction degree of the vanadium oxide system, is also observed during formation of the V_2O_{5-x} system, i.e. in the course of thermal decomposition of AMV.

As far as the results of DTA measurements are concerned, the results obtained

in argon will be presented first, because they are closer to vacuum conditions than those carried out in a stream of air. In argon three endothermic effects, corresponding to three stages of AMV decomposition, were observed (Figs 3 and 4). The first two overlapped one another, giving a broad and deformed peak. Its complex nature is more visible in the presence of TiO_2 .

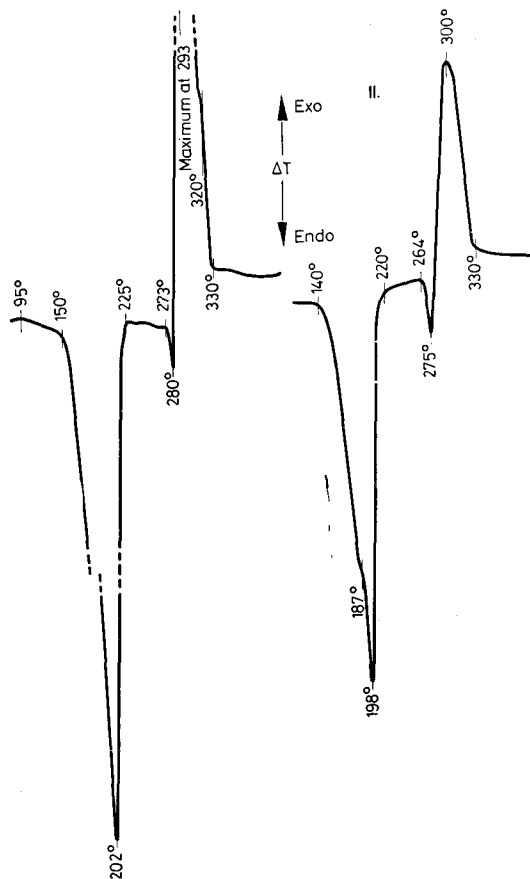


Fig. 5. DTA curves in air stream for: I — Merck preparation of AMV; II — Merck preparation of AMV + TiO_2

It may be added that the blind experiments carried out with TiO_2 showed that anatase does not give any heat effect. However, by mass- and TG-analyses, a weight loss of 0.2% was observed, mainly H_2O and CO_2 .

The next, strong endotherm (Figs 3 and 4), with a maximum at about 310° , corresponds to the third stage of decomposition (Figs 1 and 2). Here, although only a slight change in conversion degree takes place, a considerable change

occurs in the reduction degree of the vanadium oxide system and one may expect rather a high molar heat in this decomposition stage.

Between these large effects a smooth line (Fig. 3) or a complex one (Fig. 4) is observed, according to the value of the reduction degree. When this degree was small after the second stage of the decomposition, a smooth line was observed. In the opposite case, when the reduction degree was large (about 20%), complex exothermic effects appeared. Hence, these effects may be interpreted as being caused by some reactions in which a lower vanadium oxide is a reactant.

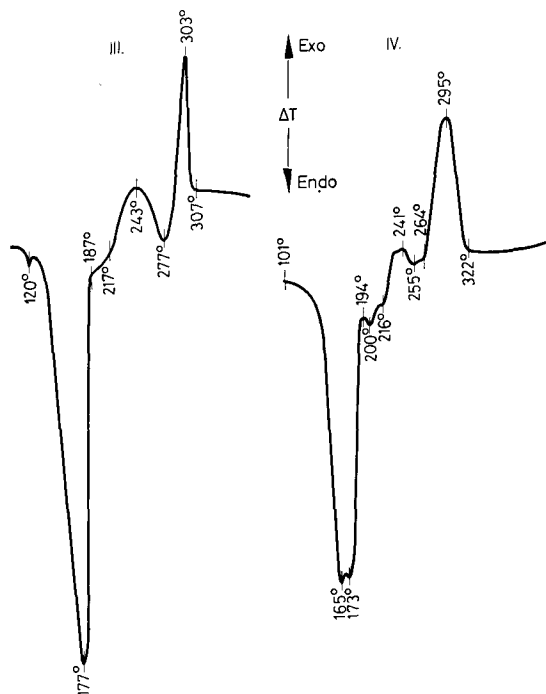


Fig. 6. DTA curves in air stream for: III — POCh preparation of AMV; IV — POCh preparation of AMV + TiO₂

Indeed, the decomposition products were mainly amorphous, but some lines of various vanadium oxides were present. If the heating is continued, some equilibration and crystallization processes occur and, as a result, the univariant phase equilibrium $V_2O_5 - V_6O_{13} - O_2$ is reached at high temperatures [15].

In the case of other AMV preparations (Fig. 3) the reduction degree of the vanadium oxide system after the second stage of decomposition is too low (about 5%) for a lower oxide of vanadium to be formed. In such a case, the exothermic effect is observed after the third stage, when the reduction degree exceeds 10%.

The DTA curves relating to the air stream (Figs 5 and 6) are very similar to those relating to the argon stream in the broad ranges of temperature and decom-

position degree. The difference appears above 270–280° and above 95–97% of the decomposition. At this point the large exotherm starts, which is undoubtedly the result of reoxidation of the V_2O_{5-x} system, as was confirmed by the increasing weight in the supplementary TG measurements. On these grounds, one may assume that not only in vacuo but also in an air atmosphere, redox reactions (2)–(4) take place in the course of AMV decomposition.

Conclusions

1. The temperature-programmed decomposition of ammonium metavanadate runs through three stages, in which the contribution of redox reactions increases successively.
2. Differences in reduction degree between various preparations of AMV are most probably caused by such textural factors as crystallinity, arrangement of crystallites in grains, their size and shape, porosity, etc.
3. The courses of the first and second stages of decomposition for a given preparation are independent of the surrounding atmosphere.
4. In the third stage the influence of the atmosphere is a decisive parameter. In vacuum and argon, successive reduction of the vanadium oxide system takes place, but in air reoxidation is observed.
5. Decomposition of NH_4VO_3 together with TiO_2 (anatase) is characterized by an increase in the redox reaction rates. As a result higher reduction degrees are reached.

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The authors wish to express their gratitude to Professor A. Bielański for his interest in this work and for valuable discussions.

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RÉSUMÉ — On a étudié, par spectrométrie de masse et par ATD, la décomposition thermique de NH_4VO_3 et des mélanges de $\text{NH}_4\text{VO}_3-\text{TiO}_2$. On a distingué trois étapes de décomposition, dans lesquelles la contribution des réactions du type redox augmentait successivement. La plus grande part de la décomposition est indépendante de la qualité de l'atmosphère, seule la troisième étape est influencée. Dans le vide dans l'argon la réduction du système d'oxyde de vanadium est continue mais dans l'air la réoxydation de celui-ci a lieu.

ZUSAMMENFASSUNG — Die thermische Zersetzung von NH_4VO_3 und $\text{NH}_4\text{VO}_3-\text{TiO}_2$ Mischungen wurde durch Massenspektrometrie und DTA untersucht. Drei Zersetzungsstufen wurden unterschieden, bei denen die Beteiligung der Reaktionen vom Redox-Typ der Reihe nach zunahm. Der größere Teil der Zersetzungsreaktionen war unabhängig von der Art der Atmosphäre, nur die dritte Stufe änderte sich hierbei. Im Vakuum und in Argon erfolgte eine kontinuierliche Reduktion des Vanadiumoxid-Systems, jedoch in Luft eine Reoxidierung.

Резюме — С помощью масс-спектрометрии и ДТА изучено термическое разложение NH_4VO_3 и смесей $\text{NH}_4\text{VO}_3-\text{TiO}_2$. Были разделены три стадии разложения, для которых вклад окислительно-восстановительных реакций последовательно увеличивался. Большая часть разложения не зависела от типа атмосферы и только третья стадия подвергалась изменению. В вакууме и в атмосфере аргона происходило непрерывное восстановление ванадий оксидной системы, но в атмосфере воздуха имело место ее обратное окисление.