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ELECTRICAL CONDUCTIVITY MEASUREMENTS DURING THE THERMAL DECOMPOSITION REACTION OF AMMONIUM METAVANADATE

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Electrical conductivity vs. temperature curve shows all characteristic peaks due to individual stages of the thermal decomposition reaction of NH_4VO_3, including the stage of formation of the anhydrous ammonium divanadate at ~150°, obtainable only under special experimental conditions on TG, DTG, and DTA curves. It is suggested that such measurements can be used for detecting and/or confirming the existence of intermediate solid products of decomposition in case they are difficult to be identified.

By applying especially chosen experimental conditions for the reaction of thermal decomposition of NH_4VO_3 to V_2O_5 in the air atmosphere it was possible to find that this reaction occurs in three stages, so that ammonium divanadate $(NH_4)_2O \cdot 2\,V_2O_5$ is formed as the first intermediate product of decomposition, ammonium trivanadate $(NH_4)_2O \cdot 3\,V_2O_5$ as the second, and V_2O_5 as the final product [1, 2]. The separation of the first stage and the isolation of the anhydrous divanadate was possible only if a relatively thin layer of the parent substance (up to 0.5 mmol/cm^2) and relatively low heating rates (25 to 150°/h) were used. If a thicker layer and/or a higher heating rate was used the first and the second stage of decomposition were merged together on both TG (or DTG) and DTA curves, thus resulting in the disappearance of the particular effect and of the plateau referring to ammonium divanadate.

The above experimental data induced the author to formulate special suggestions for reporting thermoanalytical data [3] stressing the necessity of taking into consideration the above mentioned parameters in the description of experiments. The existence of ammonium divanadate and the above mentioned conditions of obtaining it were also confirmed by Lamure and Colin [4]. Kinetic parameters for the three stages of that decomposition reaction were determined by the author using a modified Freeman and Carroll method [5]. By applying the above conditions of performing thermoanalytical measurements Stoch [6] could separate the DTA peaks of gypsum and could obtain on the DTA curve a double peak relating to the intermediate product (mesophase) in the thermal decomposition of dickite into metakaolinite. Similarly Maciejewski and Leyko [7] found that the occurrence of different basic lead carbonates during the thermal decomposition of $PbCO_3$ depends on the thickness of the layer of

the parent substance. Also a preliminary thermogravimetric study of the thermal decomposition of $Ca(NO_3)_2 \cdot 4\,H_2O$ and of the complex compound $Ca(NO_3)_2 \cdot CO(NH_2)_2 \cdot 3\,H_2O$ performed by the author and Wieczorek-Ciurowa on a Chevenard type balance showed the existence of $Ca(NO_3)_2 \cdot 3\,H_2O$ as the intermediate hydrate during the thermal decomposition of the tetrahydrate and proved better thermal stability of the complex compound as compared with the hydrated calcium nitrate and urea. Incomplete results of that study were published by Piechocińska and Wieczorek-Ciurowa [8] with the deficient description of experimental conditions.

In the present work thermoconductometric analysis (electrical conductivity measurements during heating a sample) was used for investigating the course of the thermal decomposition process of NH_4VO_3 in the air atmosphere. Such experiments seemed to be useful in the case of a complex thermal decomposition reaction as being able to deliver information relating to the changing concentration of crystal lattice defects, such changes being connected with any formation process of a new solid phase [9, 10].

Experimental

Glavkhimreaktiv pure preparation of NH_4VO_3 was used, the same as used previously [1, 2]. Its purity was checked by determining the contents of the tetravalent vanadium (titrating with $KMnO_4$ solution), sodium contents using the flame photometric method, and admixtures of heavy metals (iron and copper), magnesium, and silicon semiquantitatively using a middle-dispersion quartz spectrograph ISP – 22. The results are shown in Table 1.

Table 1

Impurity	% contents
V^{IV}	undetectable
Na	0.016
Si	0.010
Mg	0.001
Cu	0.001
Fe	0.001

The preparation was ground in an agate mortar before the experiments and the average crystal size of the unground (10 μm) and of the ground (5 μm) preparation was determined under the microscope with the micrometric eyepiece.

Electrical conductivity measurements were performed during heating 12 mm-diameter and 6 mm-thick pellets compressed under $\sim$1000 atm and placed between nickel electrodes in an electrical resistance furnace. Resistance of the sample was measured by the use of a tube megohm-meter in the range from $10^9\ \Omega$ to $2.1 \cdot 10^5$

Ω, and from $2.0 \cdot 10^5$ Ω by the compensation method using a Wheatestone bridge operated at 1000 c/s and an oscillograph as the zero-point instrument.* Temperature of the furnace was being gradually raised every 10° and a $\pm$ 0.5° precise temrature controller was used. Owing to the characteristics of the tube megohmmeter the resistance value of 10^9 Ω constituted the limit of measurability.

Results and discussion

Fig. 1 shows the results of the experiments. A decrease of conductivity in the temperature range of 20–50° (and farther below the limit of measurability) can be ascribed to a probable desorption process of water vapor from the surface of the sample. Three maxima consequently observed on the conductivity curve at the temperatures of 150°, about 190°, and 230° correspond well with the three

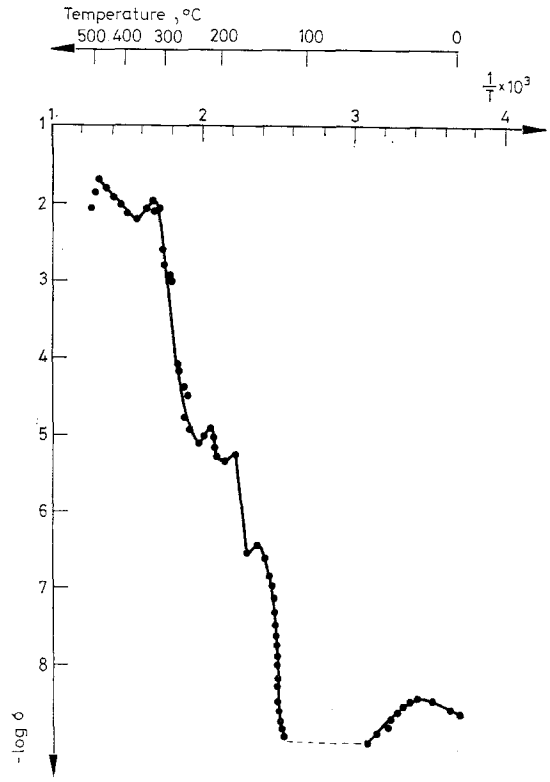

Fig. 1. Logarithm of the electrical conductivity σ (ohm) of a NH_4VO_3 sample during its thermal decomposition process vs. reciprocal absolute temperature ($1/T$, K^{-1}). Weight of the sample-0.9 g, layer thickness: 797 mg/cm^2 or 6.81 mmol/cm^2

* Measurements were performed by J. Stoch.

stages of the thermal decomposition process of NH_4VO_3, determined by the use of TG, DTG, and DTA methods [1, 2]. Decreases of the conductivity observed after peaks (maxima) in all three stages can be explained as the result of the decreasing amount of crystal lattice defects due to their diffusion and combining when nuclei of a new solid phase are formed. Consequently the conductivity increases again after this induction period when nuclei of the new phase start to grow quickly and join together. The above changes of the conductivity overlap the linear increase of the log σ due to thermal excitation.

It is characteristic that the change relating to the first stage of the reaction (decomposition of NH_4VO_3 to ammonium divanadate at 150°) detected previously on TG curves, distinctly appeared on the conductivity curve although the measurement here was performed with the use of a "thick" layer (6.81 mmol/cm^2) of the parent substance, thus under the conditions which preclude detecting this stage and obtaining the anhydrous divanadate in the course of TG, DTG, or DTA measurements [1, 2, 4].

The peak appearing on the curve (Fig. 1) in the range of temperatures of 290–370° can be related to the recrystallization process of V_2O_5 [11] as well as to the possible reaction of oxidation of V_6O_{13} to V_2O_5. The oxide V_6O_{13} can be formed here at least in trace amounts during the decomposition of ammonium trivanadate due to the possible reduction of V_2O_5 by the gaseous ammonia [2].

The above results suggest that electrical conductivity measurements during continuous heating of a solid sample can serve as a useful tool, especially for detecting and/or confirming the existence of intermediate solid products of decomposition.

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RÉSUMÉ — La courbe de la conductivité électrique en fonction de la température met en évidence tous les pics caractéristiques dus aux étapes individuelles de la réaction de décomposition thermique de NH_4VO_3, y compris celle de la formation du divanadate d'ammonium anhydre à ~150 °, qu'on n'obtient sur les courbes TG, TGD et ATD que dans des conditions d'expérience spéciales. On suggère d'utiliser ces mesures pour déceler ou confirmer l'existence des produits intermédiaires solides difficiles à identifier pendant la décomposition.

ZUSAMMENFASSUNG — Die graphische Darstellung der elektrischen Leitfähigkeit als Funktion der Temperatur weist sämtliche charakteristischen Peaks auf, welche durch die einzelnen Stufen der thermischen Zersetzungsreaktion von NH_4VO_3 bedingt werden. Inbegriffen ist die Stufe der Entstehung von wasserfreiem Ammoniumdivanadat bei ~150 °, welche an den TG, DTG und DTA-Kurven nur unter speziellen Versuchsbedingungen erhalten werden kann. Es wird angenommen daß solche Messungen zum Nachweis und zur Bestätigung der Existenz fester intermediärer Zersetzungsprodukte herangezogen werden können, falls letztere schwer zu identifizieren sind.

Резюме — Кривая зависимости электропроводности от температуры обнаруживает все пики, характеризующие отдельные стадии реакции терморазпада NH_4VO_3 — включая и стадию образования безводного диванадата аммонии при 150°, наблюдающиеся на кривых ТГ, ДТГ и ДТА только при специальных экспериментальных условиях. Высказано мнение, что такие измерения можно использовать для обнаруживания и/или подтверждения наличия промежуточных твердых продуктов распада в случаях, когда их трудно идентифицировать.