



Thermal decomposition of ammonium paratungstate tetrahydrate: New insights by a combined thermal and kinetic analysis



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ABSTRACT

The thermal decomposition of ammonium paratungstate tetrahydrate has been studied in oxidising atmosphere at four heating rates employing the analytical techniques TG, DTG, DSC, and MS. In total, three endothermic and two exothermic effects have been detected. From the combined thermal and kinetic analysis based on the MS curves of water and ammonia, the decomposition path has been characterised as a system of consecutive and competing reactions. The activation energies of the five effects for water and ammonia were discussed. On the basis of the kinetic model and the quantified MS data the stoichiometry for the whole pathway of the thermal decomposition of the title compound was construed.

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1. Introduction and historic background

Ammonium paratungstate tetrahydrate, $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$, which will be referred to as APT-4H₂O, is used worldwide as the industrial feedstock for the production of several tungsten-containing products, mostly tungsten carbides, tungsten filaments and electrodes as well as various tungsten-containing heavy alloys.

Due to its extraordinarily high solubility in water and organic solvents, ammonium metatungstate (AMT), $(\text{NH}_4)_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$, is of particular importance for fabricating numerous catalytic systems. Substrates like Al₂O₃, TiO₂, ZrO₂, CeO₂, Nb₂O₅ or polycrystalline platinum are impregnated with AMT solution and subsequently conditioned under different atmospheres at varying temperatures. AMT is produced through a fascinating method by “roasting” APT-4H₂O at 250–300 °C and spray-drying the digested solution. The detailed information about thermochemistry and kinetics of APT's thermal decomposition is of great technical and commercial significance, especially for optimising the roasting process.

Laurent proposed in the 1840s the classification of three types of tungstates, namely i) mono- (“normal”) and ditungstates,

ii) paratungstates, iii) metatungstates [1]. This notation is still in use. In the classical, but outdated oxidic notation these tungstates are written as i) M(I)₂O·WO₃ and M(I)₂O·2WO₃, ii) 5M(I)₂O·12WO₃·nH₂O, iii) 3M(I)₂O·12WO₃·mH₂O. The first study on the thermal decomposition of “ammonium tungstate” (but not yet classified according to Laurent) was published by Anthon [2] in 1836. He found that during heating of ammonium tungstate ammonia and water are liberated leaving behind “tungstic acid” or blue-coloured tungsten suboxides, depending on using open or closed crucibles.

To the best of our knowledge, the first analysis of thermal decomposition of APT-4H₂O with “modern” analytical methods goes back to the year 1956, when Muro studied it by XRD (X-ray diffraction) in ambient air at selected temperatures up to 900 °C with dwell times of up to 8 h [3]. He found that between 500 and 600 °C tetragonal WO₃ powder was formed. At the end of the 1950s Neugebauer et al. [4] studied the decomposition of “ammonium tungstate” mainly by TG (thermogravimetry) in different atmospheres. According to the provided analytical data (mass loss in air: 10.77%, WO₃: 89.14%) the compound used had the composition APT·3.2H₂O. For the first time, the thermal decomposition in air was described as a five-step process. Another pioneering work was published in 1961 by Ahn [5] who applied different methods to study the process in air and vacuum: mass loss, quantitative determination of ammonia evolved, DTA, XRD, specific surface area measurements, and electron microscopy. He stated that the crystal

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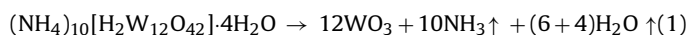
Nomenclature

a	Subindex for ammonia reaction steps (e.g., 1a for the 1st step)
AMT	Ammonium metatungstate
APT	Ammonium paratungstate
APT·2.9H ₂ O	Ammonium paratungstate 2.9 hydrate
APT·4H ₂ O	Ammonium paratungstate tetrahydrate
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Differential thermogravimetry
k	Factor for calculation of ms(NH ₃)
MS	Mass spectrometry
MS(H ₂ O)	Measured MS curve of water
ms(NH ₃)	Pure ammonia MS curve (calculated)
TA	Thermal analysis
TG	Thermogravimetry
XRD	X-ray diffraction
w	Subindex for water reaction steps (e.g., 1w for the 1st step)
A	Area in Fig. 3 (mol)
A*	Pre-exponential factor (s ⁻¹)
e	Formal concentration of educts
E	Activation energy (kJ mol ⁻¹)
K _{cat}	Order of autocatalysis
I _{meas}	Measured ion current (A)
I _{norm}	Normalised ion current (mol s ⁻¹)
j	Number of points in student value
m	Mass (kg)
m	Mass number in MS
Δm	Relative mass difference (%)
n	Amount of substance (mol)
n*	Reaction order
p	Formal concentration of products
P	Area under MS curve (As)
R	Gas constant (J K ⁻¹ mol ⁻¹)
S	Relative standard deviation (%)
T	Absolute temperature (K)
t	Time (s)
t-crit.(0.95,j)	Student value for confidence level 95% and j points
w	Mass fraction (%)
X _{max}	Maximum of liberation degree at the respective step (%)
X _{step}	Liberation degree at the respective step (%)
z	Ionic charge
α	Degree of conversion
β	Heating rate (K min ⁻¹)
ϑ	Temperature (°C)

water is completely removed below 250 °C, whereas ammonia is released in four steps by 415 °C.

Since our publication from 2008 [6] only a few studies about the thermal decomposition of APT·4H₂O have been published such as [7–10]. In addition to the standard thermal method, microwave technique [11] and mechanochemical decomposition have also been applied [12]. The thermal decomposition in a fluidised-bed reactor was described in reference [13].

It is widely accepted that the overall reaction of the thermal decomposition of APT·4H₂O can be described as



Both volatile components water and ammonia are released in several steps with different stoichiometric ratios, as emphasised in

our study [6]. According to the gross reaction (Eq. (1)), the thermal decomposition of APT·4H₂O is an example for a non-reversible reaction of the endothermic gas-solid reaction type [14]



Therefore, the decomposition of APT·4H₂O is a suitable candidate for kinetic modelling. The general objective of a kinetic analysis is i) to simulate the individual steps of the entire process by selecting appropriate mathematical models, ii) to interpret the single steps by determining specific parameters typical for the reaction, e.g. Arrhenius activation energy, pre-exponential factor, and reaction order, iii) to predict the reaction process by determining the temporal concentration trend as a function of temperature [14]. Beside the knowledge of the reaction type, an essential prerequisite for kinetic modelling is the irreversibility of the reaction (cf. Eqs. (1), (2)).

A comprehensive kinetic analysis of APT's thermal decomposition is lacking up to now. The inadequate kinetic modelling described in reference [15] was based on two assumptions: i) The decomposition reaction can be described as a sequence of consecutive reactions, where competing reactions are not permitted, ii) only the 1st order reaction type is allowed. However, the variety of reaction types cannot be restricted by this simplified approach, but can be done only by applying a multivariate kinetic analysis. The would-be study on reaction kinetics in reference [10] was limited to the calculation of apparent activation energies from TG and DTA data by using three different model-free methods.

The general significance of mass spectrometry (MS) for the analysis of evolved gases is reviewed in reference [16]. The MS analysis was applied in particular to the thermal decomposition of APT·4H₂O, sometimes in combination with other analytical methods [17–21]. However, a mass spectrometric analysis at different heating rates combined with common thermoanalytical methods is still lacking. Moreover, the MS data was not exploited in the cited publications for a kinetic analysis.

Compared to our previous investigation [6], the current study presents a more comprehensive analysis of the thermal decomposition of APT·4H₂O, including its first-time detailed kinetic analysis. The reaction types of phase transformation and kinetic parameters were determined by applying multivariate non-linear regression methods to a series of simultaneous MS measurements recorded at four heating rates in air.

2. Material and methods

2.1. Material used

Ammonium paratungstate tetrahydrate (APT·4H₂O) (Global Tungsten & Powders Corp., Towanda, USA) was characterised in detail in reference [6]. As followed from TG analysis the crystal water content amounted to 2.9 mol (see Table 2). The formula (NH₄)₁₀[H₂W₁₂O₄₂]·2.9H₂O (APT·2.9H₂O) was used throughout this study. The structure of APT·4H₂O obviously “tolerates” the deficit of 1.1 mol water without any structural changes [6].

2.2. Simultaneous techniques

The thermal analysis (TA) was performed by using the highly sensitive instrument Sensys (Setaram Instrumentation) connected via a heated capillary (120 °C) with a quadrupole mass spectrometer for the gas analysis (corundum crucible, volume: 0.1 mL, ca. 200 mg sample mass, 20 mL min⁻¹ air flow) under dynamic conditions (heating rate β: 2.0, 5.0, 9.0, and 15.0 K min⁻¹, ϑ: 30–600 °C). Ion currents of the ions with m/z equal to 15 (NH⁺), 16 (O⁺, NH₂⁺), 17 (NH₃⁺, OH⁺), 18 (H₂O⁺), 28 (N₂⁺), 30 (NO⁺), 32 (O₂⁺), 44 (CO₂⁺, N₂O⁺), and 46 (NO₂⁺) were traced. These measurements were

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