

Short communication

Surface tungsten reduction during thermal decomposition of ammonium paratungstate tetrahydrate in oxidising atmosphere: A paradox?



Martin J.G. Fait^{a,*}, Jörg Radnik^a, Hans-Joachim Lunk^b

^a Leibniz-Institut für Katalyse e.V., Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

^b 2858 Lake RD, Towanda, PA 18848, USA

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ABSTRACT

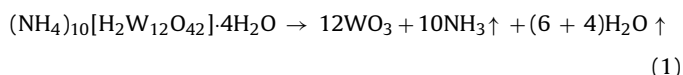
The interaction of ammonia, liberated during thermal decomposition of ammonium paratungstate tetrahydrate in oxidising atmosphere, with tungsten has been studied employing a conventional microbalance combined with MS (Setaram's instrument *Sensys*). Applying XPS a partial reduction of tungsten at the surface with the minimal tungsten oxidation number of +5.3 for a sample generated at 293 °C was detected. The balancing oxidation of ammonia to nitrogen/nitrogen oxides has been proven by MS. An amount of 0.049 mol e⁻ per mol W was transferred which resulted in an ammonia conversion degree from 2.1 mol% (NO₂ formation) to 3.0 mol% (N₂ formation).

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1. Introduction

The multi-step process, from tungsten-containing ores like wolframite and scheelite to metallic tungsten, leads to the crystallization of ammonium paratungstate tetrahydrate (NH₄)₁₀[H₂W₁₂O₄₂]·4H₂O (APT·4H₂O) as a prominent representative of the polyoxometalates [1]. A technologically important step is the thermal decomposition of APT·4H₂O, which generally is performed under reducing conditions yielding “tungsten blue oxide” (TBO). In contrast to its parent material, TBO does not represent a well-defined chemical compound, but is only the designation of a blue-coloured industrially manufactured oxidic tungsten compound [2].

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



The volatile components water and ammonia are released in several steps with different molar ratios, as emphasised e.g. in our study [3]. In addition to water and ammonia, the formation of nitrogen oxides during thermal decomposition of various

ammonium-containing compounds has been reported, as for APT·4H₂O [4,5] and the ammonium metalates (NH₄)_xM_yO_z (M = V, Cr, Mo and W) [6]. The formation of nitrogen oxides stated in reference [4] is inevitably because the experiments were carried out in platinum crucibles. Platinum is the catalyst for the combustion of ammonia to nitrous gases (Ostwald process). Its catalytic effect has been confirmed by conducting the decomposition of APT·4H₂O in platinum vs. inert corundum crucibles [3]. The reduction of WO₃ and APT·4H₂O with ammonia was studied in a microbalance by several techniques without analysing the gaseous products formed [7]. In another study of thermal decomposition of APT·4H₂O, a portion of 5 mol% NO beside 95 mol% NH₃ was postulated [5].

The objective of the present investigation was to examine the interaction of ammonia with the residual solid during the thermal decomposition of APT·4H₂O in oxidising atmosphere. The experiments were performed using Setaram's instrument *Sensys*, a combination of microbalance and mass spectrometer (MS). While MS enabled the analysis of the gaseous phase, X-ray photoelectron spectroscopy (XPS) was used to characterise tungsten's valence state.

2. Material and methods

2.1. Material

Ammonium paratungstate tetrahydrate (Global Tungsten & Powders Corp., Towanda, USA) used in this study was characterised

* Corresponding author.

E-mail address: martin.fait@catalysis.de (M.J.G. Fait).

in detail as described in reference [8]. As follows from TG analysis (mass loss: 10.62%) the crystal water content amounted to 2.9 mol. The formula $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 2.9\text{H}_2\text{O}$ (APT-2.9H₂O) was used throughout this study.

2.2. Thermal analysis combined with MS analysis

The thermal analysis (TG, DTG, DSC) was carried out using the instrument *Sensys* (Setaram Instrumentation), which combines a microbalance via a heated capillary with a mass spectrometer for the evolved gas analysis (crucible: corundum, volume: 0.1 mL; sample mass: ca. 200 mg; synthesised air or helium flow: 20 mL min⁻¹; heating rate β : 2.0 K min⁻¹). After reaching the chosen temperature (244, 293, and 342 °C), the sample was rapidly cooled down in helium to room temperature to “freeze” the tungsten oxidation state at the surface and subsequently analysed by XPS. The ion currents of the ions with m/z equal to 15 (NH⁺), 16 (O⁺, NH₂⁺), 17 (NH₃⁺, OH⁺), 18 (H₂O⁺), 30 (NO⁺), 32 (O₂⁺), 44 (N₂O⁺), and 46 (NO₂⁺) were traced.

2.3. XPS

The samples were transferred in a closed container under atmospheric conditions from the instrument *Sensys* to the XPS instrument, then locked in its UHV chamber and subsequently measured at room temperature. X-ray photoelectron spectra were recorded on a VG ESCALAB 220iXL instrument (VG Scientific) using a monochromatic Al K α X-ray beam ($h\nu = 1486.68$ eV). After Shirley background subtraction, the signals were fitted by mixed Gaussian and Lorentzian distributions. For a quantitative analysis, the peak areas were divided by element-specific Scofield factors and an analyser-dependent transmission function. The electron binding energies, E_B , are referenced to 284.8 eV (C 1s, adventitious carbon).

3. Results and discussion

The starting material APT-2.9H₂O was partially decomposed by heating in oxidising atmosphere to different target temperatures. The temperatures were defined by choosing characteristic points on the analogously shaped DSC (differential scanning calorimetry) and DTG (differential thermal gravimetry) curves (see [3]), i.e., minima at 244 °C and 293 °C and inflection point at 342 °C. The ammonia rates were the highest at 244 and 293 °C and low at 342 °C (see Fig. 3). The corresponding mass losses determined by TG amounted to 2.72, 5.29, and 8.50%. The decomposition degree $\alpha = m(\vartheta)/m(\text{ov})$ was defined as the quotient of mass loss at a specific temperature, $m(\vartheta)$, and the overall mass loss, $m(\text{ov}) = 10.52\%$. The calculated values α for the three temperatures are 0.26, 0.53, and 0.81, respectively.

3.1. XPS analysis

Ammonia from APT-2.9H₂O could be oxidised either by oxygen from ambient atmosphere or by W⁶⁺ of the solid. If ammonia reacts with the residual solid, tungsten's valence state will be decreased. The method of choice for determining the changes is XPS with an information depth of about 10 nm. In Fig. 1 the W core level XP spectra (4f and 5p_{3/2}) are presented as experimental and fitted curves for APT-2.9H₂O at room temperature and after its partial thermal decomposition at 244, 293, and 342 °C. The N 1s and W 4d spectra are shown in the Supplementary material, Figs. S1 and S2.

The numeric results of peak deconvolution focused on W 4f_{7/2} electron levels are presented in Table 1 as binding energies E_B and the percentages of integrated intensities x . In addition the calculated oxidation numbers n^* are given. The calculation method of n^*

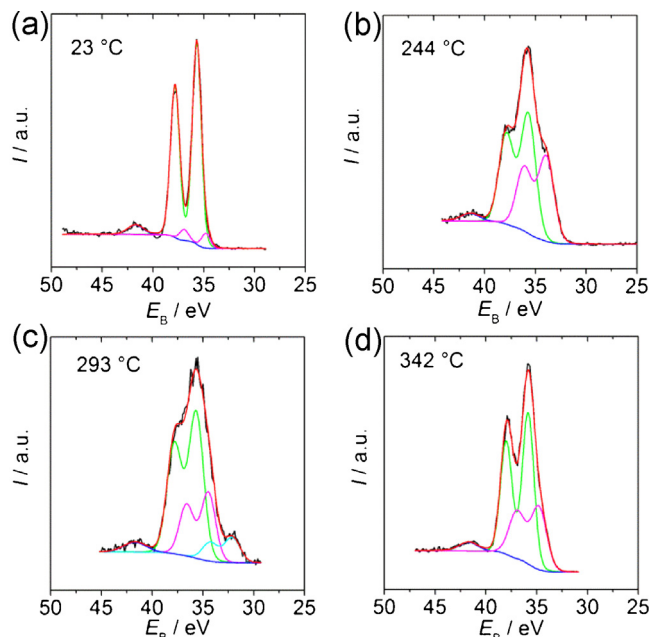


Fig. 1. Experimental (black) and fitted W core level spectra (red) of APT-2.9H₂O samples before (a) and after partial thermal decomposition in air at 244 (b), 293 (c), and 342 °C (d) (β : 2 K min⁻¹). The individual peaks are coloured according to the tungsten valence state and the electron levels: blue: W 5p_{3/2} {W(VI)}; green: W 4f_{5/2}, W 4f_{7/2} {W(VI)}; magenta: W 4f_{5/2}, W 4f_{7/2} {W(V)}; cyan: W 4f_{5/2}, W 4f_{7/2} {W(II)} (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1

Assignment of tungsten valence states and binding energies (E_B /eV) of W 4f_{7/2} electron levels, relative amounts of valence state (x /mol%), and calculated oxidation numbers (n^*), for samples generated from APT-2.9H₂O by its partial thermal decomposition at 244, 293, and 342 °C in air, compared to the parent material at 23 °C.

ϑ (°C)	W(VI)			W(V)			W(II)		
	E_B	x	n^*	E_B	x	n^*	E_B	x	n^*
23	35.7	93.4	5.9	34.8	6.6	5.3	–	–	–
244	35.7	57.2	5.9	34.0	42.8	4.8	–	–	–
293	35.7	61.2	5.9	34.5	27.8	5.1	32.2	11.0	2.2
342	35.8	64.2	6.0	34.9	35.8	5.4	–	–	–

is illustrated in Fig. S3, Supplementary material. In brief, two interpolation curves E_B vs. valence state were generated using published data for W, WO₂, and WO₃ [9]. The recalculation of the experimental data for E_B (W 4f_{7/2}) on the basis of these curves provided n^* .

The complete data of numeric results of peak deconvolution of W core level spectra (4f and 5p_{3/2}) is presented in Table T1, Supplementary material. In summary, four different tungsten signals were distinguished which are marked by different colours according to the tungsten valence state and the electron level (cf. Fig. 1).

Based on n^* the binding energies could be assigned to the valence states W(VI) and W(V) for the parent compound as well as for the partially decomposed samples. The fact that the parent material contained a minor portion of W(V) was a surprise. However, the goodness-of-fit was higher when W(V) was included ($\chi^2 = 1.800$ with W(V) in comparison to 2.014 without W(V), see Fig. S4, Supplementary material). The small amount of W(V) can be explained by a minor reduction of W(VI) under X-ray exposure in vacuum.

The molar fractions of nitrogen of the samples generated at 244, 293, and 342 °C amounted to 8.83, 6.91, and 6.05 mol%. The corresponding ammonia concentrations 0.79, 2.71, and 3.57 mol%

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