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## **Thermal decomposition of ammonium tetrathiotungstate**

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### **Keywords**

(NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>, WS<sub>3</sub>, WS<sub>2</sub>, WO<sub>3</sub>, TG/DTA, MS, XRD, FTIR, SEM

### **Abstract**

The thermal decomposition of ammonium tetrathiotungstate (ATT), (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> was studied by SEM, FTIR, XRD, EDX and TG/DTA-MS. The decomposition of ATT involved three steps in inert atmosphere: (i) release of free water between 30-140 °C; (ii) formation of an amorphous WS<sub>3</sub> phase between 170-280 °C, from which (iii) a slightly crystalline WS<sub>2</sub> formed between 330-470 °C. As a difference compared to inert atmosphere, in air in the second step the ATT decomposed into directly WS<sub>2</sub> instead of WS<sub>3</sub>. This WS<sub>2</sub> phase was amorphous, and still contained traces of ATT. Between 260-

500 °C from the WS<sub>2</sub> monoclinic tungsten oxide crystallized in two steps: at 302 °C a slightly crystalline m-WO<sub>3</sub> formed, which became more crystalline at 471 °C. During the investigation of the effect of the particle size, it was found that the thermal behaviour of ATT crystals was similar to ATT powder, with some shift in the decomposition temperature. The XRD results showed that the WS<sub>2</sub> formed from the ATT powder in N<sub>2</sub> had a higher level of crystallization, compared to the WS<sub>2</sub> obtained from ATT crystals.

## 1. Introduction

Ammonium tetrathiotungstate (ATT, (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>) is an important material as a precursor for WS<sub>3</sub> [1-4], WS<sub>2</sub> [4-11] and different tetraalkylammonium thiotungstates [7, 12-17]. ATT is an important industrial lubricant as-well [18]. Tetraalkylammonium thiotungstates are precursors for WS<sub>2</sub> catalysts [7, 15-17]. WS<sub>2</sub> can be also used as gas sensor [6,19-20], dry lubricant [21,22] and in lithium batteries [23-25].

WS<sub>2</sub> catalysts are promoted mostly with cobalt or nickel and used in hydrodesulfurization (HDS) reactions [26-28]. HDS is the central process to remove sulphur from crude oils. There are several ways to prepare these catalysts, like comaceration [29], homogeneous sulphide precipitation [14], hydrothermal and solvothermal processes [30-34], solution reactions [35,36] and thiosalt decomposition [37-39]. With the decomposition of thiotungstates a high sulphur content can be achieved in the final WS<sub>2</sub> catalysts [40,41]. Also the controlled composition and wide ranges of achievable surface areas [6,42-45] made this method promising for preparing WS<sub>2</sub> catalysts. The thiotungstate precursors can be activated by ex situ or in situ methods. The ex situ method means, that the precursor is activated under a H<sub>2</sub>/H<sub>2</sub>S gas flow, by heating it to 400 °C with 4 °C min<sup>-1</sup>, and then keeping the material at this temperature for 4 h. In situ activated catalysts are prepared by thermal decomposition of the precursors at 350 °C with 10 °C min<sup>-1</sup>, 3.1 MPa in H<sub>2</sub> atmosphere [5].

Because of the importance of these preparation methods, it is crucial to have detailed knowledge the thermal decomposition of the various thiotungstate precursors. The thermal behaviour of different tetraalkylammonium thiotungstates was investigated previously in detail [7,9,10,15,16,39,46-48], but in case of the ATT only some studies can be found [5,49,50]. In 1970 Voorhoeve et al [49] investigated the decomposition of ATT in vacuum and H<sub>2</sub> flow by X-ray diffraction (XRD), differential thermal analysis (DTA), optical microscopy and electron spin resonance (ESR). The results showed that ATT decomposed in two steps, and the temperature of the steps depended on the pressure, but did not depend on the particle size in the 50-2000 µm range. In the first step (ca. 120-300 °C) an amorphous

tungsten sulfide phase formed in an endothermic process with a composition of  $WS_{2.6-3.3}$ , which crystallized into  $WS_2$  at 300-400 °C in an exothermic process.

The other two studies are more recent. Espino et al. [5] characterized the decomposition in  $N_2$  flow with thermogravimetric (TG), and DTA measurements. Their results also showed that ATT decomposed in two steps. The first step occurred at ca. 190-280 °C when  $WS_3$  was formed in an endothermic reaction, and  $NH_3$  and  $H_2S$  evolved in this step. Then at ca. 340-410 °C the as-formed  $WS_3$  decomposed into  $WS_2$  in an exothermic reaction. The composition of the annealing products and the quality of the evolved gases were calculated from the experimental mass losses.

Yi et al. investigated the decomposition of ATT in  $N_2$  as well by TG, temperature-programmed decomposition with mass spectroscopy (TPD-MS), in situ FTIR and Raman spectroscopic measurements [50]. In the first step (175-250 °C)  $WS_3$  formed, while  $H_2O$ ,  $H_2$  and  $NH_3$  evolved, then at 350-400 °C  $WS_2$  formed accompanied with the loss of sulphur.

The need for our research was that, to best to our knowledge, there had been no previous detailed study on the thermal behaviour of ATT in air. In this study we aimed to get more information on the thermal decomposition of ATT both in air and in inert atmospheres, characterize the intermediates and investigate the effect of the particle size of ATT. For this thermal analysis (TG/DTA-MS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used.

## 2. Experimental

The ATT material was obtained from Alfa-Aesar, which had the composition of  $(NH_4)_2WS_4$  (CAS:13862-78-7).

SEM images and EDX data were obtained by a JEOL JSM-5500LV scanning electron microscope.

Powder XRD patterns were recorded on a PANalytical X'pert Pro MPD X-ray diffractometer using  $Cu K_\alpha$  radiation.

FTIR spectra were measured by an Excalibur Series FTS 3000 (Biorad) FTIR spectrophotometer in the range of 400-4000  $cm^{-1}$  in KBr pellets.

TG/DTA measurements were performed on an STD 2960 Simultaneous DTA/TGA (TA Instruments Inc.) thermal analyzer using a heating rate of 10 °C  $min^{-1}$  and Pt crucibles. The thermobalance was purged either with air or nitrogen (130  $ml min^{-1}$ ). Evolved gas analytical (EGA) curves were recorded by a Thermostar GSD 200 (Balzers Instruments) quadrupole mass spectrometer (MS). A mass range between  $m/z = 1-64$  was monitored through 64 channels in Multiple Ion Detection Mode (MID) with a

measuring time of 0.5 s channel<sup>-1</sup>. Further details of the TG/DTA-MS setup are described elsewhere [51,52]

### 3. Results and discussion

#### 3.1 Characterization of the ATT material

According to the SEM images the ATT material was built up mainly by ca. 200-500 µm plain crystals (Fig. 1.A), while there were some larger, ca. 2.5 mm crystals as well (Fig. 1.B). In the FTIR spectrum of ATT (Fig. 2) the O-H deformation and stretching vibrations of the water molecules absorbed on the surface of ATT were present around 1636 cm<sup>-1</sup> and 3215 cm<sup>-1</sup> respectively, while the N-H deformation and stretching vibrations of the NH<sub>4</sub><sup>+</sup> ions were visible at 1390 cm<sup>-1</sup> and 3120 cm<sup>-1</sup> respectively [50]. The peak at 850 cm<sup>-1</sup> was assigned to the W=S vibration, and the peak at 460 cm<sup>-1</sup> to the W-S vibration [47].

In order to investigate the effect of the particle size some of the ATT was powdered. The ATT powder was identified with powder XRD measurement (Fig. 3), and the result was identical to the PDF 076-0751 card. According to the SEM images the ATT powder consisted of ca. 0,5-3 µm particles (Fig. 1.C), which aggregated into larger, 20-40 µm blocks (Fig. 1.D).

#### 3.2 Thermal decomposition of the ATT powder in nitrogen

The ATT powder decomposed in three steps in nitrogen atmosphere. In the first step (30-140 °C) the mass decrease was 0.3 %, and a small amount of water evolved (Fig. 4). This was physically absorbed water, because there was no change in the XRD pattern (Fig. 3). The water evolution was showed by an endothermic peak at 76 °C, and by the MS curve of 18<sup>+</sup> (H<sub>2</sub>O).

The second step occurred at 170-280 °C, with a mass decrease of 18.7 %. This decomposition step was accompanied with an endothermic process and with the release of H<sub>2</sub>S and NH<sub>3</sub> (Fig. 4). The MS curves also showed that part of the evolved NH<sub>3</sub> and H<sub>2</sub>S combusted, resulting in N<sub>2</sub>O (44<sup>+</sup>), SO (48<sup>+</sup>), SO<sub>2</sub> (64<sup>+</sup>) and H<sub>2</sub>O (18<sup>+</sup>). This combustion was possible, because even in the N<sub>2</sub>-purged furnace there were traces of O<sub>2</sub>. Previously H<sub>2</sub> evolution was reported instead of H<sub>2</sub>S at this temperature range [50], but our results did not confirm this. The FTIR results (Fig. 2) also showed the NH<sub>3</sub> evolution, as the N-H peaks at 1390 cm<sup>-1</sup> and 3120 cm<sup>-1</sup> disappeared completely. In this step an amorphous tungsten trisulphide was formed as reported before [5,49]. This amorphous state could be seen from the XRD

pattern (Fig. 3) as well. The composition of this phase was close to  $WS_3$ , i.e. by TG (Fig. 4) the observed mass loss (18.7 %) was close to the theoretical one corresponding to  $WS_3$  (19.5 %). EDX also confirmed the composition; however, with larger error, as the measured W:S ratio was 1:2.3-3.5 instead of the theoretical 1:3.

In the third step (330-470 °C) the amorphous  $WS_3$  transformed into a slightly crystalline  $WS_2$  (Fig. 3), while sulphur evaporated. The MS curves revealed that the evolved sulphur combusted into SO ( $48^+$ ) and  $SO_2$  ( $64^+$ ), the main combustion product being  $SO_2$ . The XRD proved the crystallization as at 800 °C a slightly crystalline  $WS_2$  phase was detected. The measured mass loss (27.64 %) was close to the theoretical mass loss corresponding to  $WS_2$  (28.75 %). This transformation was accompanied with an exothermic peak on the DTA curve (Fig. 4), as both the crystallization of  $WS_2$  and the combustion of as-released sulphur are exothermic processes. The transformation into  $WS_2$  could be also seen in the FTIR spectrum, as the region below  $1200\text{ cm}^{-1}$  altered significantly (Fig. 2).

### 3.3 Thermal decomposition of the ATT powder in air

In the first decomposition step (30-120 °C), there was no difference between the thermal behaviour of ATT powder in air and inert atmospheres (Fig. 4-5).

Between 180-260 °C the ATT started to decompose, and similar to the decomposition in nitrogen this step was accompanied by an endothermic process as  $H_2S$  and  $NH_3$  were released (Fig. 5). The MS curves showed that some of the  $H_2S$  and  $NH_3$  burnt into SO,  $SO_2$  and NO [53-56]. The XRD, FTIR and SEM-EDX results revealed that ATT partially decomposed (only 15.54 % mass loss instead of the theoretical 28.75 %), and from it directly  $WS_2$  was obtained. The XRD pattern showed (Fig. 6) that part of the phase was amorphous  $WS_2$ , and also traces of ATT could be found ( $17.27^\circ$ ,  $18.49^\circ$ ,  $28.92^\circ$  and  $31.53^\circ$ ). In the FTIR spectrum (Fig. 7), some of the peaks were assigned to the ATT ( $462\text{ cm}^{-1}$ ,  $841\text{ cm}^{-1}$  and  $1397\text{ cm}^{-1}$ ), while the other peaks to the  $WS_2$  ( $462\text{ cm}^{-1}$ ,  $516\text{ cm}^{-1}$ ,  $946\text{ cm}^{-1}$  and  $1604\text{ cm}^{-1}$ ). On the SEM images it can be seen, that this intermediate contained particles of different sizes. The smallest particles were ca. 1-5  $\mu\text{m}$ , while there were some larger ca. 15-150  $\mu\text{m}$  particles (Fig. 8.A). On the surface of the larger particles there were cracks (Fig. 8.B), which probably formed during gas release. According to the EDX results, most of the smaller particles were  $WS_2$  (W:S ratio 1:2) and the larger particles were ATT (W:S ratio 1:4).

At higher temperature (260-500 °C) the as-obtained intermediate transformed completely into monoclinic tungsten oxide (PDF 89-4476) (Fig. 6). The m- $WO_3$  crystallized in two steps, at 302 °C a slightly crystalline  $WO_3$  was formed (Fig. 6), which became more crystalline at higher temperature

(471 °C). During this transformation sulphur evaporated, which burnt into SO and SO<sub>2</sub>. This transformation was accompanied by a very intense exothermic peak on the DTA curve as both the crystallization and the combustion of the evolved sulphur were exothermic processes.

### 3.4 Comparison of the thermal behaviour of ATT powder and crystals

The TG/DTA curves of the ATT crystals (Fig. 9) were basically identical to the curves of ATT powder. The mass loss values for ATT crystal and powder in the first, second and third decomposition steps were almost the same. At the second step the decomposition temperature of the powder was lower, than in case of the crystal. On the other hand the decomposition temperature of the third step was not influenced by the particle size.

The FTIR results were identical in case of the powder and crystal. The XRD results were similar too, the only difference was that the WS<sub>2</sub> formed from the ATT powder in N<sub>2</sub> had a higher level of crystallization (Fig. 10).

## 4. Conclusion

The thermal behaviour of the ammonium tetrathiotungstate was studied by SEM, FTIR, XRD, EDX and TG/DTA-MS.

The thermal decomposition of ATT powder involved three steps in inert atmosphere: (i) release of free water between 30-140 °C, and (ii) formation of an amorphous WS<sub>3</sub> phase between 170-280 °C in endothermic reactions. In this step NH<sub>3</sub> and H<sub>2</sub>S evolved, however H<sub>2</sub> evolution could not be detected as written before [50]. Some of the NH<sub>3</sub> and H<sub>2</sub>S combusted into H<sub>2</sub>O, N<sub>2</sub>O, SO and SO<sub>2</sub>. (iii) Between 330-470 °C a slightly crystalline WS<sub>2</sub> formed from the WS<sub>3</sub> in an exothermic process. During this process sulphur evaporated, which burnt into SO and SO<sub>2</sub>.

As a difference compared to inert atmosphere, in air in the second step an amorphous WS<sub>2</sub> was formed instead of WS<sub>3</sub>. This WS<sub>2</sub> phase still contained traces of ATT as-well. Between 260-500 °C from this mixture monoclinic tungsten oxide crystallized in two steps.

The thermal behaviour of ATT crystals was similar to the powder, with some shift in the decomposition temperature. The main difference between them was in the XRD results, which showed that the WS<sub>2</sub> formed from the ATT powder in N<sub>2</sub> had a higher level of crystallization.

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## Figures

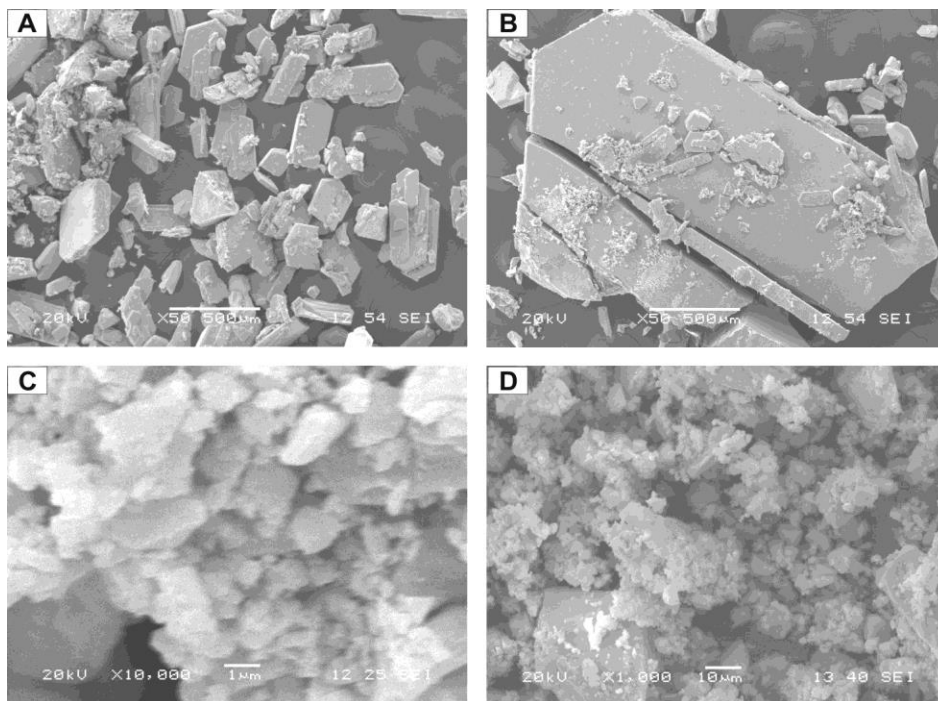


Figure 1. SEM images of the ATT crystals (A, B) and powder (C,D)

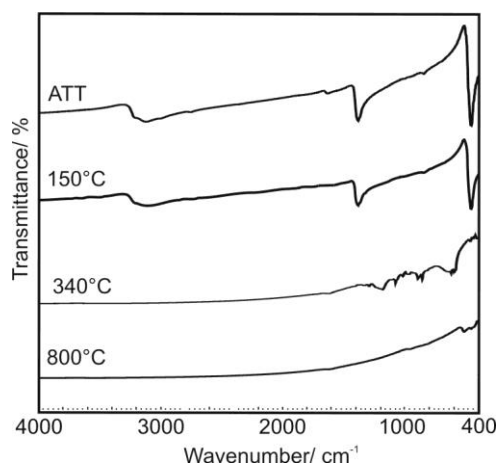


Figure 2. FTIR spectra of the thermal decomposition products of ATT powder in N<sub>2</sub>

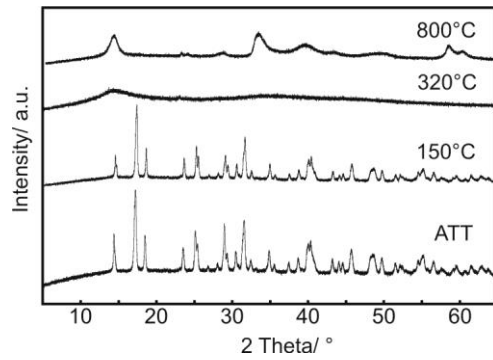


Figure 3. XRD patterns of the thermal decomposition products of ATT powder in N<sub>2</sub>

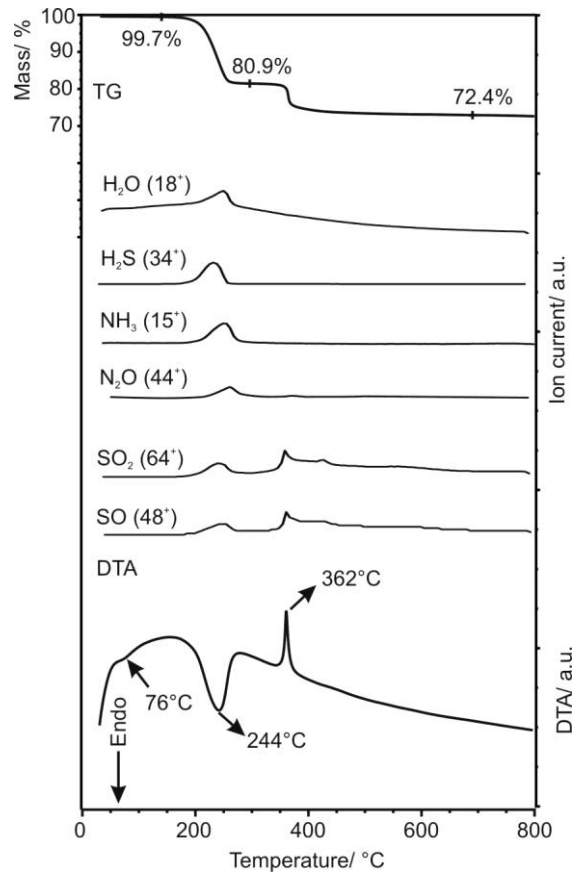


Figure 4. TG/DTA and evolved gas analytical MS ion current curves of the thermal decomposition of ATT powder in N<sub>2</sub>

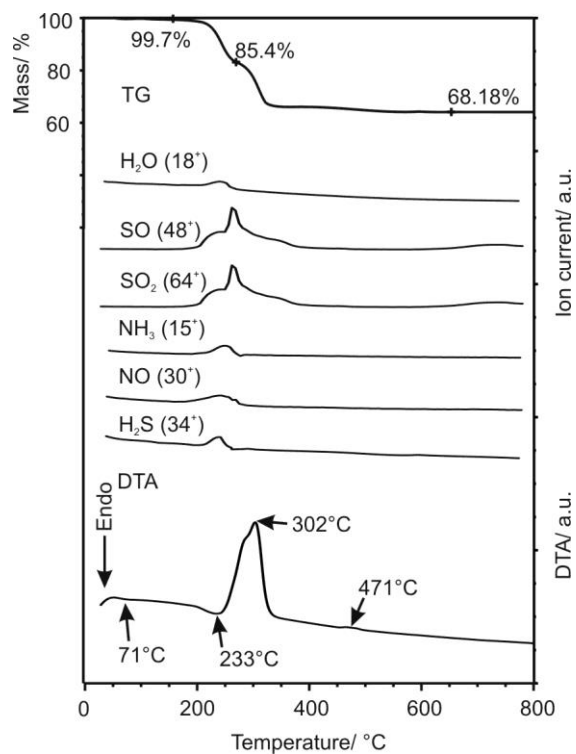


Figure 5. TG/DTA and evolved gas analytical MS ion current curves of the thermal decomposition of ATT powder in air

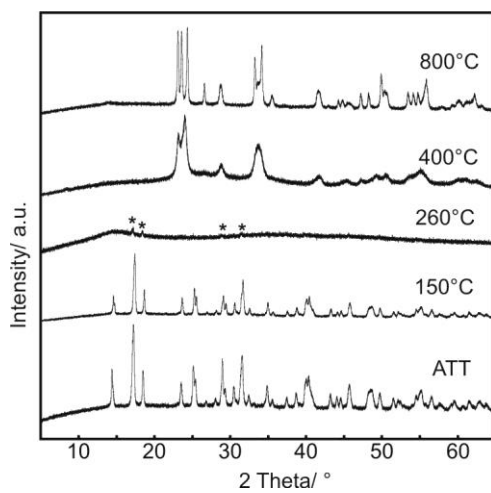


Figure 6. XRD patterns of the thermal decomposition products of ATT powder in air, \*: ATT peaks

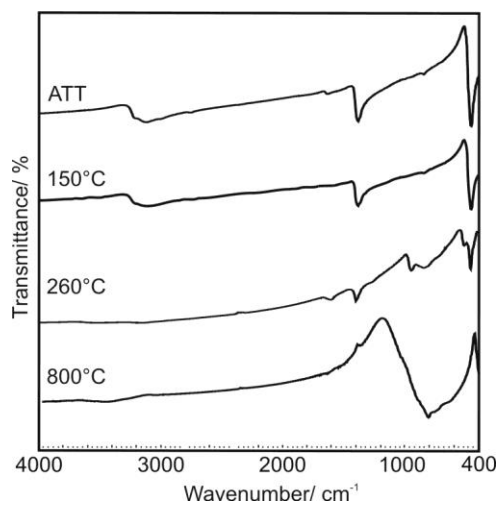


Figure 7. FTIR spectra of the thermal decomposition products of ATT powder in air

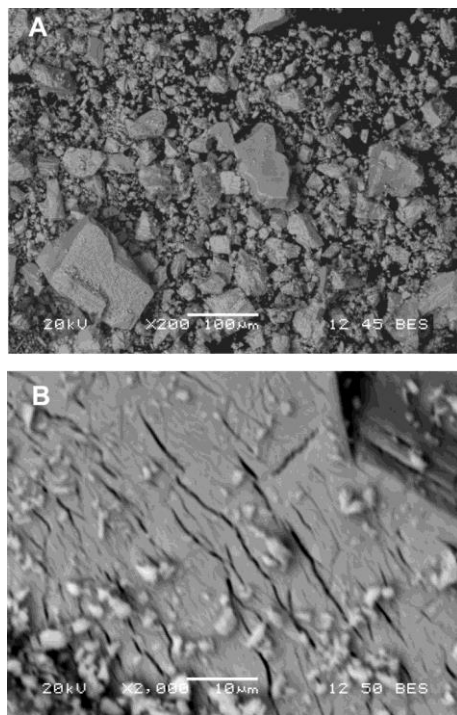


Figure 8. SEM images of the as-obtained mixture at 260°C in air

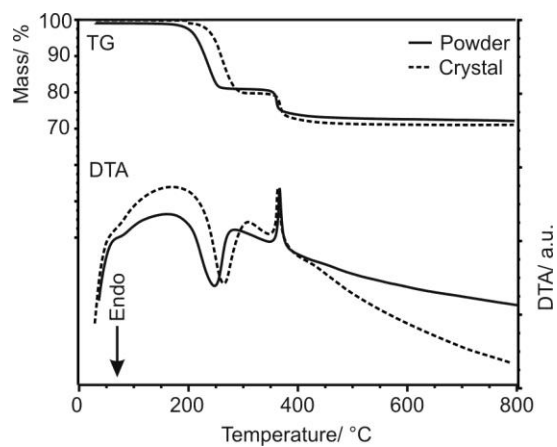


Figure 9. TG/DTA curves of the thermal decomposition of ATT powder and crystals in N<sub>2</sub>

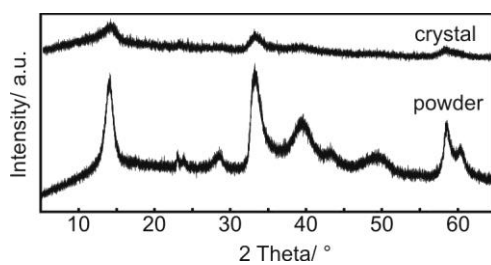


Figure 10. XRD patterns of the as-formed WS<sub>2</sub> from the ATT powder and crystals in N<sub>2</sub> at 800 °C