Thermochimica Acta 546 (2012) 1–7

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The investigation of thermal decomposition mechanism of ammonium phosphotungstate hydrate in inert gas atmosphere

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A R T I C L E I N F O

Article history:
Received 8 May 2012
Received in revised form 16 July 2012
Accepted 17 July 2012
Available online 24 July 2012

Keywords:
Ammonium phosphotungstate hydrate
Thermal decomposition
Tungsten oxide
Phosphotungstate bronze
Thermal analysis

A B S T R A C T

In this study, TGA–DTA–MS and TGT techniques were used to investigate the thermal decomposition of ammonium phosphotungstate hydrate ($(NH_4)_3(PW_{12}O_{40})\cdot xH_2O$, APhT) in inert gas (Ar) atmosphere. The thermal decomposition products of APhT obtained in Ar atmosphere at various temperatures were characterized by using XRD, FT-IR and SEM analyses.

APhT losses its crystal water in the first step and forms anhydrous ammonium phosphotungstate ($(NH_4)_3(PW_{12}O_{40})$, anhydrous APhT). Anhydrous APhT is stable up to 640 K and it is transformed into cubic structured, dark blue colored phosphotungstate bronze ($(PO_2)_2(WO_3)_{24}$, PhTB) which is stable up to 1250 K. PhTB is then decomposed gradually into light black colored WO_3 and $(PO)_2(WO_3)_{16}$ mixture. This mixture does not vaporize until 1423 K. After this temperature, sublimation takes place followed by melting at 1545 K and weight loss is observed due to evaporation. At 1573 K the samples are transformed into light black colored tungsten suboxide (WO_{3-y}).

1. Introduction

In conventional tungsten production processes, ammonium paratungstate hydrate (APT) is an intermediate product. APT decomposes by calcination to WO_3. Tungsten powder is obtained by H_2 reduction of WO_3. In the early 1950s, tungsten blue oxide (TBO) has replaced WO_3 [1]. TBO is used as raw material for the production of non-sag tungsten. TBO is actually a mixture of tungsten oxide, tungsten suboxides and ammonium tungsten bronze [2]. TBO is doped with K, Al and Si before H_2 reduction [3].

Gurmen et al. [4] proposed a hydrometallurgical process for the production of W metal powder from scheelite ($CaWO_4$) concentrate. First, $CaWO_4$ was dissolved in HCl solution that contains H_3PO_4 as chelating agent which forms PhTA. NH_4Cl is then added to this leach solution to precipitate APhT.

Gurmen et al. [5] studied the thermal decomposition of APhT in air atmosphere only by using TGA–DTA thermal analysis techniques. It was concluded that APhT released H_2O and NH_3 between 311 and 436 K and 6% weight loss was observed in TGA. It was also commented that phosphorus was released as P_2O_5 at 885 K according to the exothermic peak in DTA. During the formation of decomposition products of APhT at 923, 1023, 1123, 1223 and 1323 K for 2 h holding time the weight losses were increased to 9.6% and the colors of the decomposition products were changed from dark green, green, light green, bright green to yellowish-green. They pointed out that APhT contains 9 mol of crystal water, the decomposition products contain few impurities and WO_3 that is obtained from calcination of APhT has been found to have applications in powder metallurgy and other similar areas.

In our previous work [6], the thermal decomposition of APhT under non-isothermal conditions in air atmosphere was investigated in detail by TGA–DTA–MS, TGT and its decomposition products were characterized by XRD, FT-IR and SEM analytical techniques. It was determined that APhT decomposed in two steps. In the first decomposition step, APhT lost its crystal water and formed anhydrous APhT. In the second decomposition step, the anhydrous APhT was transformed to green colored tetragonal structured phosphotungstate ($P_2O_5(WO_3)_{24}$) which was stable up to 1282 K. As the temperature was increased, $P_2O_5(WO_3)_{24}$ was decomposed gradually to the oxide mixture consisting of green colored monoclinic structured WO_3 and orthorhombic structured $P_2O_5(WO_3)_{18}$. The final decomposition product obtained after thermal analysis up to 1573 K was monoclinic structured WO_3.

Von Varfolomeev et al. [7] studied the thermal decomposition of Keggin structured hetero polytungstic acids (boro, silico and phospho) by high temperature X-ray powder diffraction (HT-XRD) and high temperature infrared spectroscopy (HT-IR). It was shown that phosphotungstic acid hydrate ($H_3(PW_{12}O_{40})\cdot xH_2O$, hydrous PhTA) contained 6 mol of crystal water. They explained the characteristic IR bands of hydrous PhTA. It was determined by HT-XRD that hydrous PhTA maintained its crystal structure up to 423 K and it contained 3–6 mol of crystal water. Between 423 and 523 K, a

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http://dx.doi.org/10.1016/j.tca.2012.07.018

second cubic structure was stable. Above 523 K, crystal water was lost and the anion in the form of Keggin structure was beginning to break down. At 893 K, the decomposition was complete and the product was P_2O_5 alloyed tetragonal structured WO_3. This transformation temperature was determined to be 878 K.

In industrial applications, various types of furnaces and batch heights are used during thermal decomposition of charges. The gases evolved during these processes may purge the furnace atmosphere, which may then form inert or reducing atmosphere. In thermal decomposition of APhT, NH_3 and its decomposition products N_2 and H_2 can be produced which can generate inert or reducing atmosphere. Therefore, the products that are formed under inert or reducing atmosphere may differ from the products that are obtained in air atmosphere. For example, in industrial applications, TBO is formed during thermal decomposition of ammonium paratungstate hydrate (APT). It is therefore important to clarify the thermal decomposition mechanism of APhT under inert or non-oxidizing atmospheres. In this study, the thermal decomposition of APhT in inert gas atmosphere (Ar) was investigated by TGA–DTA–MS, thermo-gas titration (TGT) and the products obtained by thermal decomposition of APhT were also characterized by XRD, FT-IR and SEM.

2. Experimental

In our previous work [6], the preparation of APhT has been explained in detail. In the present study, horizontal furnace (Gero, F70-500/13) was used to obtain the decomposition products of APhT in Ar atmosphere at different temperatures. Quartz tube with gas inlet and outlet was placed inside the furnace. Sample was placed inside a cylindrical alumina holder which was placed at the bottom of the quartz tube. Linear heating rates and isothermal conditions were obtained by the thermocouple placed right next to the sample and by the PID unit of the temperature controller (Gero). The experimental conditions were chosen as $0.083\,K\,s^{-1}$ linear heating rate, $16.7\,mL\,s^{-1}$ gas flow rate and 1 h holding time. During the experiments, Ar was passed continuously through the system. At the end of the experiments, the system was cooled down to room temperature while gas was still purged. Thermal decomposition products were obtained at 523, 923, 1123 and 1323 K.

In order to determine NH_3 release temperature and the quantity of NH_3 evolved during reaction, TGT analysis was conducted. For this purpose, the furnace was heated at $0.083\,K\,s^{-1}$ linear heating rate and Ar was purged at $16.7\,mL\,s^{-1}$ gas flow rate. Gas absorption bottle was connected to the gas outlet of the system which contained pure water for the absorption of NH_3. The amount of NH_3 released during the thermal decomposition of APhT and dissolved in water was determined quantitatively by titration using 0.01 N HCl solution in the presence of methyl orange indicator. In order to carry out complete solubility of NH_3 produced during reaction, the out coming gas was passed through a ceramic disc which contained micro pores and the solution was stirred continuously with a magnetic stirrer.

Thermal analysis of APhT was carried out in TGA–DTA equipment (TA SDT Q600). In the experiments, 100 mg spectroscopic analysis purity samples were placed in alumina crucibles. The gas flow $1.67\,mL\,s^{-1}$ was chosen. The linear heating rates 0.042, 0.083 and $0.167\,K\,s^{-1}$ were selected. As reference sample empty alumina crucibles were used. In order to determine the types of gases released during the thermal analysis, quadrupole mass spectrometer (MS) (Pfeiffer Thermostar GSD 301 T3) was coupled to the TGA–DTA system by a meter long isolated capillary tube, which was heated to 473 K. The characterization of phases, the analysis of grain size and morphology and the determination of bond types of APhT and its thermal decomposition products were performed by XRD (Philips 1710) using Cu-Kα monochromatic X-ray ($\lambda = 1.5406\,Å$), SEM (Jeol JSM 5600) and FT-IR (ATI Unicam Mattson 1000) analytical techniques, respectively. KBr was used to prepare discs for FT-IR measurements.

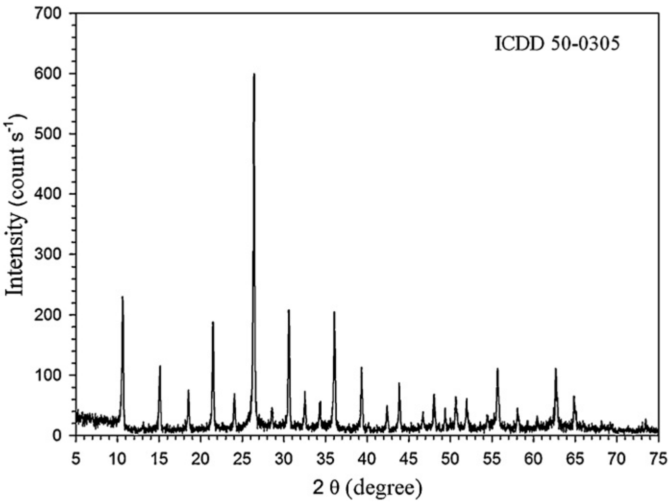

Fig. 1. XRD diagram of APhT.

3. Results and discussion

XRD diagram of synthetically prepared $CaWO_4$ contains the peaks of pure $CaWO_4$ given by the powder diffraction file number ICDD 72-0257. This diagram was given in our previous study [6]. XRD diagram of APhT (Fig. 1) is in perfect agreement with APhT diagram (ICDD 50-0305) where the chemical formula is given as $(NH_4)_3(PW_{12}O_{40})\cdot 9\cdot 5H_2O$. Gurmen et al. [5] had proposed that one mole of APhT contained 9 moles of crystal water. SEM image shows that some part of APhT particles have 1–2 μm diameter and most of the remaining particles consists of sub-micron spherical particles (Fig. 2).

TGA diagrams of APhT obtained in Ar atmosphere at 0.042, 0.083 and $0.167\,K\,s^{-1}$ heating rates show three steps of weight loss (Fig. 3a). The first weight loss is observed between room temperature and 465 K where APhT loses its crystal water according to the Reaction (1).

$$(NH_4)_3(PW_{12}O_{40})\cdot xH_2O \rightarrow (NH_4)_3(PW_{12}O_{40}) + xH_2O \qquad (1)$$

As seen in Fig. 3a, an average of 4.20% weight loss is observed in TGA diagram of APhT in the first decomposition step for all three

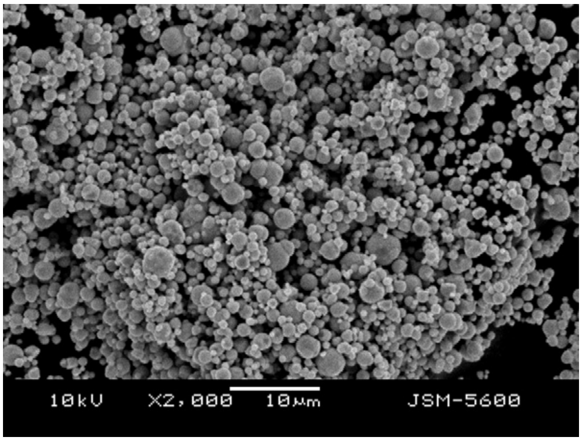

Fig. 2. SEM image of APhT.