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Investigating the solid–gas phase reaction between WO_3 powder, NH_3 and H_2O vapors to prepare ammonium paratungstate

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ABSTRACT

The solid–gas phase heterogeneous reaction between tungsten oxide powder, ammonia and water vapors was studied with the aim of preparing ammonium paratungstate (APT, $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot xH_2O$ ($X = 4, 10$)). The effects of the composition, crystal structure and particle size of the WO_3 powder were investigated along with the effect of the partial pressure of ammonia and water vapor on the products. The as-prepared APT was characterized with powder XRD, FTIR, Raman, SEM, TEM and TG/DTA-MS measurements. At 43.40 kPa and 12.23 kPa ammonia partial pressures after one day two partially reduced intermediates, i.e. W_5O_{14} and $(NH_4)_2W_2O_7\cdot 0.5H_2O$, were identified, which transformed into APT·$4H_2O$ in 30 days with a yield of almost 100%. $(NH_4)_2W_2O_7\cdot 0.5H_2O$ was produced for the first time ever, while for W_5O_{14} this was a new preparation route, as it was only produced in great vacuum at high temperature before. At 1.56 kPa ammonia partial pressure APT·$10H_2O$ was also a product of the reaction. At lower ammonia partial pressures the reaction was very slow, and only small changes were detected in the structure after 30 days. The results showed that this novel synthesis of APT is not sensitive to the reaction conditions, in contrast to the previously only available wet chemical crystallization process. According to the measurements, the as-produced APT is equivalent to the commercial ones. As an additional feature, our method is capable to yield APT nanoparticles for the first time, which is important for both research and industry due to the greater surface area.

1. Introduction

The ammonium paratungstate (APT), $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot xH_2O$ ($X = 4, 7, 10$) is the most important starting material in the tungsten industry, where usually its most stable APT·$4H_2O$ form is used [1]. From APT tungsten oxides, tungsten carbides or tungsten metal can be prepared. Among others, tungsten oxides are widespread catalysts [2–5], photocatalysts [6–10] and gas sensors [11–18]. Tungsten carbide products are also used as catalysts [19,20], but their another important application field is being the hard component in cutting and drilling tools [21–23]. Tungsten metal is applied in lightning industry [1,24–28], steel metallurgy [29,30], sporting and medical equipments [31,32] and electronics [32].

Today APT is produced by the wet chemical process [1], which is a multi-step method. The first step is the alkaline digestion, when the tungsten content is extracted from the tungsten ore concentrates, scrap metal or oxides [33]. The next step is the purification of the gained sodium tungstate solution. The type and concentration of the contaminants can vary; the typical contaminating ions are silicate, phosphate, arsenate, molybdate, fluoride, lead, bismuth and aluminum. The separation is started with silica precipitation, where the silica, phosphate and fluoride ions are separated by adding aluminum sulfate or magnesium sulfate to the solution. After that sulfide-forming cations like arsenic, molybdenum, antimony, bismuth, cobalt, etc are separated by adding sodium sulfide to the solution [33]. The third step is the ion exchange, when the sodium ions are replaced by ammonium ions. First an organic solvent is added with phase transfer catalyst to the aqueous solution, so that the tungstate content is moved to the organic phase. After that aqueous ammonia solution is added to the separated organic phase. At the end of this step an aqueous solution of ammonium isopolytungstate is obtained [34,35], from which the APT is produced by crystallization. During the evaporation of the solution,

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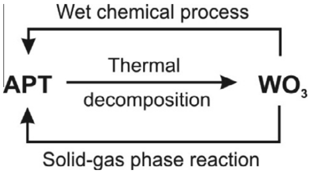

Fig. 1. Scheme of the digestion experiment.

ammonia and water are volatilized. As the pH of the solution decreases and the WO_3 concentration increases at the same time, paratungstate A ion, $[HW_6O_{21}]^{5-}$ is formed, which transforms into paratungstate B ion, $[H_2W_{12}O_{42}]^{10-}$ in an equilibrium reaction. The ammonium salt of the paratungstate B ion has the lowest solubility at these conditions, hence $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ ($APT\cdot 4H_2O$) crystallizes [36,37].

Because of its importance the production of APT has been studied for several decades, therefore the wet chemical process has been explored in detail. Nevertheless it has several disadvantages, e.g. it is very sensitive to the conditions, especially to the pH. In addition, the process has a large chemical and energy requirement [1].

The solubility of WO_3 is good in concentrated alkaline and ammonia solution. Therefore it is also used in the wet chemical process to produce APT [1]. However, it has been unknown, how NH_3 and H_2O vapors can react with WO_3, and whether they can digest it. Our main goal was to explore this reaction (Fig. 1).

Therefore, in the present study APT was produced with a solid–gas phase heterogeneous reaction between WO_3 powder, NH_3 and H_2O vapors. The effects of the reaction conditions on the products were examined: the composition, crystal structure and particle size of the WO_3 powder and the partial pressure of the ammonia vapor. Then the as-prepared APT was characterized thoroughly, by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermal analysis (TG/DTA-MS). Based on our results the properties of the as-obtained APT are identical to the commercial APT materials, also this is the only method to prepare nanosize APT.

2. Experimental

2.1. Preparation of the WO_3 starting materials

As a reference material, commercial ammonium paratungstate ($APT\cdot 4H_2O$) was obtained from H. C. Starck GmbH. The WO_3 powders prepared from the reference APT and from hexagonal ammonium tungsten bronze (HATB, $(NH4)_{0.33-x}WO_{3-y}$) were used as precursors in the solid–gas phase reactions. HATB was obtained by heating APT at 400 °C in H_2 for 6 h [38]. The precursor tungsten oxides with different compositions (oxidized or partially reduced), structures (monoclinic (m-WO_3) or hexagonal (h-WO_3)) and particle sizes (70–90 or 100–300 nm) were prepared by thermal decomposition from APT or HATB by controlling the annealing temperature and atmosphere [39]. The details of preparations are summarized in Table 1.

According to SEM images (Fig. 2), the precursor tungsten oxides (**1**, **2**, **5**–**8**) produced from APT consisted of ca. 100–300 nm particles (Fig. 2a), which aggregated into 30–100 μm blocks (Fig. 2b). While the precursor oxides (**3**, **4**, **9**–**11**) obtained from HATB were built up by ca. 70–90 nm particles (Fig. 2c), which also aggregated into 30–200 μm blocks (Fig. 2d).

2.2. Solid–gas phase reactions

The reactions between the precursor tungsten oxide powders and the NH_3 and H_2O vapors were carried out at room temperature in a sealed plastic box. WO_3 powder and aqueous ammonia solution were placed separately into the box, where the reagents were able to react only via the gas phase. The partial pressures of ammonia and water vapor were controlled by varying the concentration of ammonia in the solutions (Table 1). The equilibrium partial pressure of NH_3 and H_2O vapors values were calculated from the concentrations of the aqueous solutions [40]. Using precursors **1**–**4** the effects of the composition and crystal structure of the tungsten oxides were investigated. From precursors **5**–**11** the effects of the particle size of the powders and the partial pressure of the ammonia were studied.

In each reaction 500 mg WO_3 powder and 25 ml aqueous ammonia solution were used.

The yield of the reactions was calculated from the mass difference before and after the reaction.

2.3. Analytical methods used for the characterization

Powder XRD patterns were recorded on a PANalytical X'pert Pro MPD X-ray diffractometer using Cu Kα 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.

Raman spectra were measured by a Jobin Yvon Labram spectrophotometer equipped with an Olympus BX41 microscope in

Table 1
Preparation conditions of WO_3 precursor powders by annealing APT or HATB starting materials, and the conditions of the solid–gas phase reactions between the as-produced precursor powders and NH_3 and H_2O vapors.

Entry Nr.	Preparing WO_3 precursor powders for the solid–gas phase reactions				Conditions of the solid–gas phase reactions			
	Starting material	Atmosphere	Temperature (°C)	Particle size (nm)	Precursor powder structure	Aqueous ammonia solution concentration (M)	NH_3 pressure (kPa)	H_2O pressure (kPa)
1	APT	air	600	100–300	m-WO_3	13	43.40	1.37
2	APT	nitrogen	600	100–300	m-WO_3 partially reduced	13	43.40	1.37
3	HATB	air	600	70–90	m-WO_3	13	43.40	1.37
4	HATB	air	470	70–90	h-WO_3	13	43.40	1.37
5	APT	air	600	100–300	m-WO_3	0.1	0.15	2.34
6	APT	air	600	100–300	m-WO_3	1	1.56	2.28
7	APT	air	600	100–300	m-WO_3	0.5	0.77	2.32
8	APT	air	600	100–300	m-WO_3	6	12.23	1.97
9	HATB	air	600	70–90	m-WO_3	0.1	0.15	2.34
10	HATB	air	600	70–90	m-WO_3	1	1.56	2.28
11	HATB	air	600	70–90	m-WO_3	0.5	0.77	2.32