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Spectro-thermal investigation of the decomposition intermediates developed throughout reduction of ammonium paratungstate

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Abstract

The thermal decomposition course of ammonium paratungstate (APT) in hydrogen was studied using thermogravimetric and differential thermal analyses. X-ray diffractometry, infrared spectroscopy and diffuse reflectance spectroscopy were used to characterize and identify the intermediate solid products. It was found that ammonium paratungstate decomposes to tungsten metal W^0 through five main steps encompassing different tungsten intermediate compounds. Ammonium tungsten bronze $(NH_4)_{0.33}WO_3$, which precedes the formation of WO_3, is relatively the most stable intermediate (250–550°C) encountered through reduction of APT to tungsten metal W^0. The influence of hydrogen spillover on the reduction behavior commences to be effective just after formation of the bronze intermediate.

Keywords: Ammonium paratungstate; Tungsten bronze; Tungsten oxides; Reduction; TG

1. Introduction

As a precursor of tungsten-based catalysts [1], ammonium paratungstate (APT) received a great deal of attention to explore its thermal decomposition course to the onset of WO_3 formation. The later oxide is frequently considered as the active phase in tungsten-based catalysts [2,3]. However, for preparing supported metal catalysts, supports are directly impregnated with an aqueous solution of APT, followed by the subsequent calcination and/or reduction.

The thermal decomposition course of APT in air and nitrogen, to the onset of formation of WO_3, was the subject matter of some studies whether to characterize the thermal decomposition behavior or to estimate the different kinetic parameters for the decomposition steps [2–4]. In this laboratory, reduction of WO_3 was studied, adopting the isothermal and non-isothermal techniques, to probe the autocatalytic effect induced during the reduction process [5] and to specify the kinetic model of the reaction governing such solid/gas reduction process [6]. However, decomposition of APT in hydrogen was studied non-isothermally to estimate the different kinetic parameters controlling the decomposition process [4]. The decomposition course and identification of the intermediate compounds was beyond the aim of that study.

Ammonium tungston bronze has attracted considerable attention over the years because of its unique crystalline structure [7]. Alkali and ammonium tungsten bronzes approach the composition $A_{0.3}WO_3$ which contains two types of structural channels [8]. The first channel is a broad hexagonal one and is

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occupied by A atom, whereas the trigonal narrow one can be predestined to the insertion of guest small species as hydrogen or lithium forming for example $H_xA_{0.3}WO_3$. Ammonium tungsten bronze can be prepared by the hydrothermal reduction of APT, where both a prolonged time and a higher pressure are required [7]. It was also prepared [9] hydrothermally by the reaction of tungsten trioxide and ammonium hydroxide at high temperature (700°C). It is also reported that ammonium tungsten bronze can be prepared by reduction of APT with hydrogen [10].

In this paper our aim is to follow up the non-isothermal reduction of APT with hydrogen and to specify the different reaction intermediates aiming at defining the temperature regime at which ammonium tungsten bronze is stable.

2. Experimental

2.1. Materials

Ammonium paratungstate (APT), $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 7H_2O$ was a >99% pure product of Fluka (Switzerland). It was used as provided, without any prior pretreatment. In order to prepare the reduction intermediates, APT was heated inside a special quartz reactor in a flowing hydrogen (50 ml $\min^{-1}$) at temperatures 200°C, 350°C and 600°C for 2 h. Hydrogen gas used for reduction was a 99% pure product of the Egyptian Company of Industrial gases (Cairo, Egypt).

2.2. Thermal analysis

Thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded on heating up to 800°C at 5°C $\min^{-1}$ heating rate in a flowing atmosphere of hydrogen (30 ml $\min^{-1}$), using a 30H Shimadzu thermal analyzer. For DTA measurement, a highly sintered α-Al_2O_3 was used as the thermally inert reference.

2.3. X-ray diffractometry

XRD powder diffractograms were recorded with a model D5000 Siemens diffractometer provided with a copper anode generating Ni-filtered CuK_α radiation ($\lambda = 1.5418$ Å). Diffractograms were recorded in the 2θ range 10–80°, with a divergence slit of 1°. For phase identification purposes, an on-line data acquisition and handling system facilitated an automatic JCPDS library search and match (Diffrac software, Siemens).

2.4. Diffuse reflectance spectroscopy

Diffuse reflectance spectroscopy (DRS) spectra were measured with a Shimadzu 2100 UV–Vis spectrophotometer. Spectra were recorded over a wavelength range from 200 to 800 nm, using barium sulfate as a reference material.

2.5. Infrared spectroscopy

IR spectra were recorded using 580B Perkin–Elmer double beam spectrophotometer adopting the KBr technique. Lightly loaded wafers were analyzed over the frequency range 4000–200 cm^{-1} at a resolution of 5.3 cm^{-1}.

3. Results and discussion

The TG and DTA curves recorded on heating APT, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 7H_2O$, in flowing hydrogen at 5°C $\min^{-1}$ heating rate, are given in Fig. 1. TG curve shows that APT decomposed in four mass loss processes. It shows an additional gradual mass loss process in the temperature range 250–550°C. Correspondingly, DTA curve shows seven thermal events maximized at 120°C, 190°C, 260°C, 340°C, 380°C, 620°C and 730°C. All these thermal events are of endothermic character, except those at 340°C and 380°C, which correspond the onset of the gradual weight loss process, are exothermic.

As the first mass loss process is corresponded with two endothermic peaks at 120°C and 190°C, it seems that this step is of a composite nature. The mass loss accompanying this step (ca. 3%) suggests that it can be attributed to loss of both physisorbed and crystallization water [2–4].

X-ray diffractogram (Fig. 2) of the decomposition product obtained at 200°C, just after the first mass loss step (I in Fig. 1), suggests the formation of $(NH_4)_{10}(W_{12}O_{42})\cdot 5H_2O$, and thus revealing the dehydration process. The expected mass loss accompany-

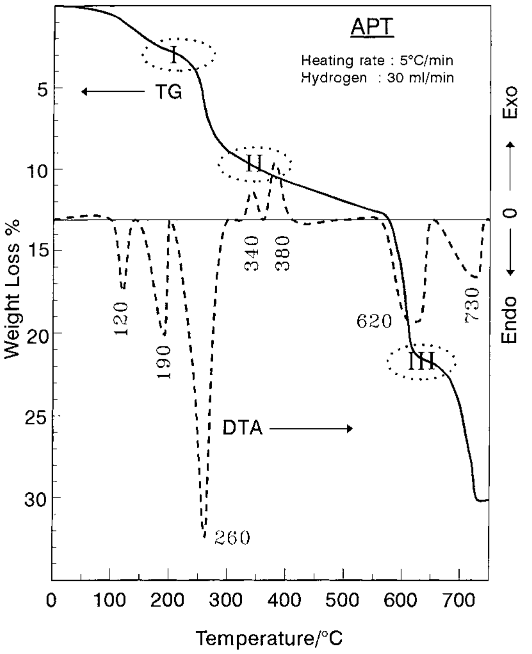

Fig. 1. TG and DTA curves recorded on heating ammonium paratungstate in flowing hydrogen atmosphere (30 ml min^{-1}) at heating rate 5°C min^{-1}.

ing such transformation is about 1.7%, which is considerably lower than the mass loss accompanied the first step (3%). This leads to the conclusion, that decomposition of APT goes further beyond the formation of the detected intermediate. This may find a support in the IR measurements (not given), where the 200°C-decomposition product reproduced the spectrum of the untreated APT with only a little decrease in the intensities of the absorption bands at 3600–2800 cm^{-1} (ν of OH and NH bonds), and at 1650 and 1400 cm^{-1} (δ of OH and NH bonds, respectively).

The second mass loss process (Fig. 1) maximized at 260°C, is also of endothermic nature and it brings the total mass loss to about 10%. A close inspection indicates that this step is ended just at the onset of the subsequent gradual mass loss exothermic process. Because of this notable interference, it is difficult to determine the precise mass loss. However, the decomposition product (II in Fig. 1) obtained at temperature regime in-between these two steps (350°C) exhibits solely the diffractograms (Fig. 2) of ammonium tungsten bronze of the composition $(NH_4)_{0.33}WO_3$. The expected mass loss due to the formation of this bronze

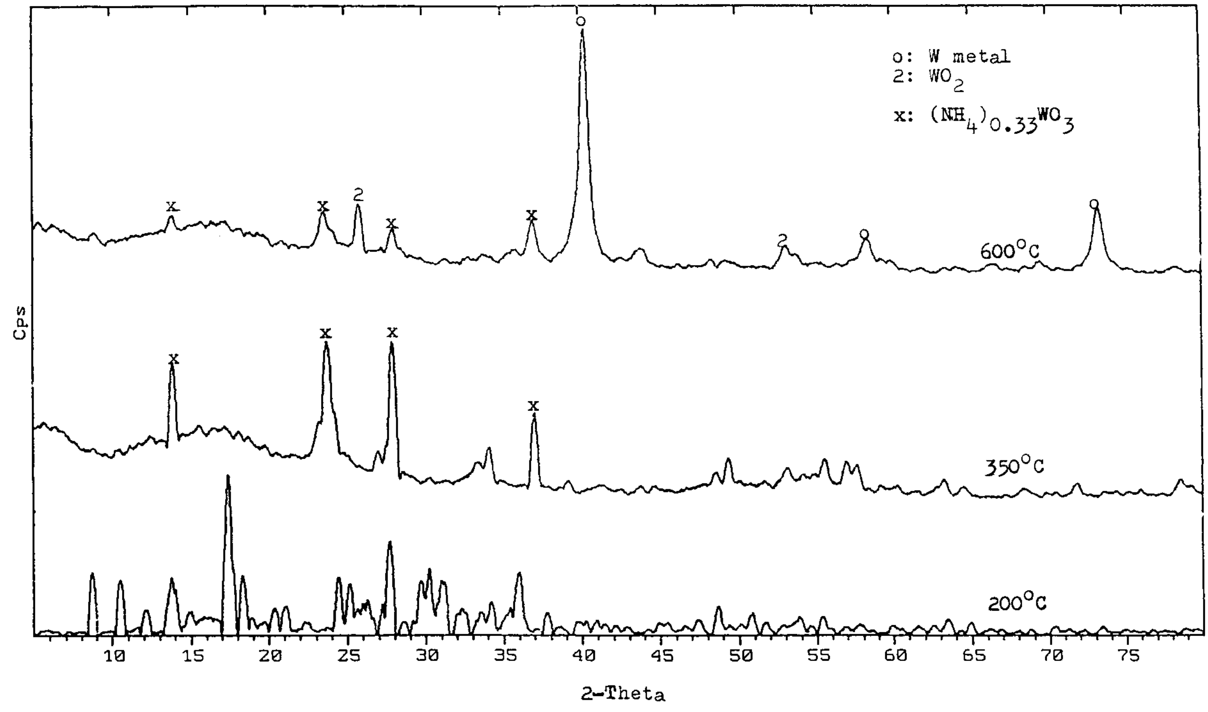

Fig. 2. X-ray diffractograms of the indicated decomposition products obtained on heating APT in flowing hydrogen atmosphere.

is 10.4%, which is more close to the experimentally determined one (10%). In support, IR results inferred the formation of this compound, where the obtained spectrum indicates the collapse of the band structure attributed to the tungstate. Furthermore, it still shows the characteristic ν and δ absorption modes of NH_4^+group at 3400 and 1400 cm^{-1}, respectively.

The structure of ammonium tungsten bronze $(NH_4)_{0.33}WO_3$ reveals that it exposes tungsten cations of lower valency than that existed in the parent APT (W^{6+}). As a matter of fact, such reduction processes may help to develop some sort of d–d electron transitions, through creation of partially filled tungsten cations. DRS spectrum (Fig. 3) recorded for the 350°C-decomposition product shows clearly that heating APT at 350°C has greatly influenced its DRS spectrum. A very broad band of high absorbency in the wavelength range 450–800 nm, indicating the d–d transitions, is observed. Moreover, the spectrum of the 350°C-decomposition product is remarkably different from that recorded for pure WO_3 (Degussa product). In agreement, XRD confirmed the formation of $(NH_4)_{0.33}WO_3$ as sole phase (Fig. 2), where no WO_3 phases were detected in the diffractogram of the 350°C-decomposition product. Hence, it can be concluded that formation of WO_3 is mostly beyond this temperature (i.e., >350°C).

Fig. 1 shows that continuous heating of APT over the temperature range 300–575°C caused a slow and gradual increase in the total mass loss till about 12.5%. This mass loss corresponds the transformation of the bronze $(NH_4)_{0.33}WO_3$ into WO_3 (total 12.6%). DTA curve (Fig. 1) shows that the commencement of this gradual weight loss process is corresponded with two exothermic effects at 340°C and 380°C, where some sort of interaction between the formed bronze and hydrogen atmosphere is expected.

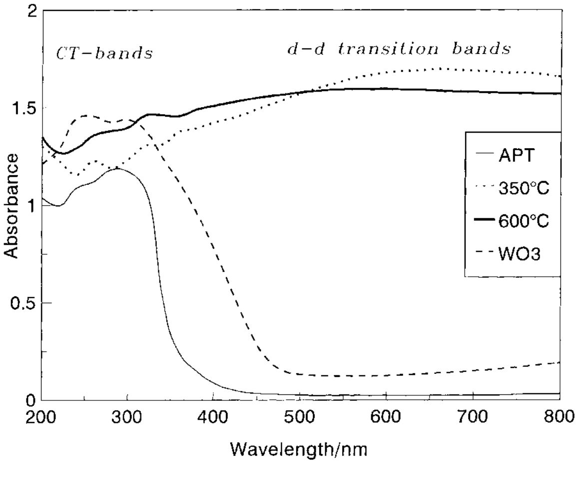

Fig. 3. DRS spectra of the indicated decomposition products obtained on heating APT in flowing hydrogen atmosphere. Spectra of APT parent and WO_3 are given for comparison.

Insertion of hydrogen into tungsten bronzes having the formula $A_{0.3}WO_3$ (A = K, NH_4 and Cs), which is known for the channel structure, to form $H_xA_{0.3}WO_3$ was the subject of a recently published work [8], where the "hydrogen spillover" technique was adopted. They reported that both the amount of hydrogen inserted and the rate of insertion is indirectly proportional to the size of the first guest A. So, for ammonium tungsten bronze $(NH_4)_{0.3}WO_3$, the coinsertion compound is represented by $H_{0.06}(NH_4)_{0.3}$-WO_3. Compared to alkali ions, which are firmly built in the lattice as interstitial defects in K- and Cs-tungsten bronzes, it is reported that insertion of hydrogen in ammonium tungsten bronze is facilitated due to the equilibrium $NH_4^+ \rightarrow NH_3 + H^+$.

Accordingly, the interaction between the produced ammonium tungsten bronze and hydrogen atmosphere may be responsible for the slow and gradual process observed at temperature range 300–575°C, where spilled and inserted hydrogen initiates such reaction. It is worth noting that this interaction may result at the end of step in the formation of hydrogen–tungsten–bronze H_xWO_3. It is reported earlier [5,6] that reduction of WO_3 is initiated with the formation of this hydrogen–tungsten–bronze.

Accumulation of the hydrogen spilt over the freshly generated tungsten sites may be responsible for the sharp and strong endothermic weight loss process maximized at 620°C. It brings the total mass loss to ca. 21%. This value is considerably higher than that expected for WO_2 formation (18.7%). This means that the reduction process is proceeded beyond the formation of WO_2. Fouad et. al [5] has previously observed that reduction of WO_3–WO_2 is almost accompanied with the earlier creation of metallic W^0. XRD diffractogram (Fig. 2) demonstrates the coexistence of this metallic W^0 phase in the decomposition product (**III** in Fig. 1) obtained at 600°C. The corresponding XRD diffractograms in Fig. 2 shows that the 600°C-decomposition product contains a mixture of phases, its predominance can be arranged as follows:

$$W^0 >>> WO_2 > (NH_4)_{0.33}WO_3 >> WO_3$$

The remarkable predominance of the metallic W^0 phase reflects, in fact, the influence of "hydrogen spillover" on the reduction process [6]. The notable decrease in the WO_3 phase may help to suggest the complete transformation of this phase to WO_2, revealing also the important role of the spiltover hydrogen, or, in contrast, it indicates that most of the ammonium tungsten bronze converted directly to WO_2. This suggestion may be inferred through the considerable coexistence of $(NH_4)_{0.33}WO_3$ phase (XRD-detected) in the 600°C-decomposition product, and this reflects the relative thermal stability of this compound. In accordance with XRD results, the DRS spectrum of the 600°C-decomposition product demonstrates the coexistence of different tungsten compounds which exposes tungsten cations of different valencies. It also shows a broad absorption band with high absorbance at the d–d transition region (450–800 nm).

The last and final mass loss step (Fig. 1) maximized at 730°C and brings the total mass loss to 30.2% which is more close to 30.7% expected from the complete reduction of APT to metallic tungsten W^0.

4. Conclusions

The above presented and discussed results helped to conclude that the decomposition of APT in hydrogen proceeds according to the following scheme:

1. APT, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 7H_2O$ dehydrates to $(NH_4)_{10}(W_{12}O_{42})\cdot 5H_2O$ at temperature range 100–200°C.
2. $(NH_4)_{10}(W_{12}O_{42})\cdot 5H_2O$ decomposes into $(NH_4)_{0.33}WO_3$ at temperature range 200–250°C.
3. $(NH_4)_{0.33}WO_3$ shows a relative stability at temperature range 250–575°C, although it suffers a very slow mass loss process resulting in the partial transformation into $H_{0.33}WO_3$ and/or WO_3.
4. These suggested compounds are reduced directly to WO_2 and metallic tungsten at 600°C, where complete reduction into metallic tungsten is achieved at about 730°C.

Hydrogen spillover has greatly influenced the reduction behavior of APT to W^0. This effect can be clearly demonstrated after $(NH_4)_{0.33}WO_3$ formation, which shows a relative thermal stability in a wide temperature range.

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