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REACTION MECHANISM OF $Fe_8V_{10}W_{16}O_{85}$ SYNTHESIS

J. Walczak, I. Rychlowska-Himmel and P. Tabero

Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastow 42
71-065 Szczecin, Poland

Abstract

The reaction mechanism of the synthesis of $Fe_8V_{10}W_{16}O_{85}$ was studied by means of XRD, IR spectroscopy and DTA techniques. It was found that the intermediate in the reaction may be either $FeVO_4$ or $FeVO_4$ admixed with an unidentified phase X, depending on the reaction temperature. The IR spectrum of the phase $Fe_8V_{10}W_{16}O_{85}$ is reported for the first time.

Keywords: DTA, IR, reaction mechanism, XRD

Introduction

Previous studies of the system Fe_2O_3–V_2O_5–WO_3 revealed a new compound $Fe_8V_{10}W_{16}O_{85}$ [1, 2]. This phase can be obtained as a result of the following reactions:

$$4Fe_2O_3 + 5V_2O_5 + 16WO_3 = Fe_8V_{10}W_{16}O_{85} \quad (1)$$

$$8FeVO_4 + V_2O_5 + 16WO_3 = Fe_8V_{10}W_{16}O_{85} \quad (2)$$

$$4Fe_2WO_6 + 5V_2O_5 + 12WO_3 = Fe_8V_{10}W_{16}O_{85} \quad (3)$$

Up to 923 K, $FeVO_4$ is the sole reaction product. However, at 973 K the phase $Fe_8V_{10}W_{16}O_{85}$ appears, accompanied by an unidentified phase X [2].

This paper presents the results of an investigation of the reaction mechanism of the synthesis made from mixture of Fe_2O_3, V_2O_5 and WO_3 (Eq. (1)). XRD, IR spectroscopy and DTA were used as measurement techniques.

Experimental

The reagents used in the experiments were: V_2O_5, an a.p. product of POCh (Gliwice, Poland); α-Fe_2O_3, an a.p. product of VEB (Germany), previously calcined at 1273 K in four 48 h cycles; WO_3, 99.9%, (Fluka AG, Switzerland); KBr, used in IR spectroscopic measurements; $FeVO_4$ and $Fe_8V_{10}W_{16}O_{85}$ were obtained by earlier-described procedures [2, 3].

The basic examinations were performed on an X-ray diffractometer Dron 3 (Bourevestnik, St. Petersburg, Russia). The radiation source was a cobalt tube with an iron filter.

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An initial mixture for the whole experimental series was prepared by weighing Fe_2O_3, V_2O_5 and WO_3, in a molar ratio of 4:5:16 and grinding the mixture for 45 min in a mechanical agate mortar. Samples of 1.5 g were placed in crucibles and heated at the given constant temperature in a silite furnace. After a fixed time, the samples were removed from the furnace, cooled to ambient temperature and ground for 5 min in an agate mortar. The samples were then examined by X-ray phase diffraction, IR spectroscopy and DTA. The intensities and angular positions of diffraction lines were recorded by a stepwise technique (step 0.02° 2θ, t=1 s).

IR spectra between 1400 and 300 cm^{-1} were recorded on a Specord M 80 IR spectrometer (Carl Zeiss Jena, Germany) using a halide disc technique. In all measurements, the substance was mixed with KBr in a proportion of 1:300.

For the DTA measurements, between 273 and 1273 K, a Paulik-Paulik-Erdey derivatograph (MOM, Budapest, Hungary) was used. 1000 mg samples were placed in quartz crucibles and heated at a rate of 10 K min^{-1}.

Results and discussion

The measurements were carried out at 973, 993, 1013 and 1033 K. The DTA curve of the initial mixture exhibits three endothermic peaks, at 923, 1053 and 1188 K. The peak at 923 K is undoubtedly related to melting of a mixture containing V_2O_5 [2]. A similar endothermic peak appears in the DTA curves of samples heated at 1033 K for 15, 60 or 180 min. However, they are absent when the sample is heated at 1033 K for 480 min or longer. On the other hand, such an effect at about 923 K can be observed even in the DTA curves of samples that contain less than 1 mol% of free V_2O_5 [2]. Such amounts of V_2O_5 are impossible to detect by means of XRD. Therefore, it can be assumed that, at temperatures above 923 K, at least in the early stage, the reaction will proceed in the presence of a certain amount of a liquid phase. After heating at given temperatures, all samples were sintered, but not molten.

The results of X-ray phase analysis allow the distinction of two stages in $Fe_8V_{10}W_{16}O_{85}$ synthesis. During the first stage, lasting not longer than 15 min at any temperature, the intermediate found in the reaction mixture is $FeVO_4$ (accompanied by unchanged WO_3). The reflections characteristic of V_2O_5 disappear. In consequence of the very high reaction rate and the low intensity of the diffraction lines characteristic of $FeVO_4$, this reaction stage was not investigated thoroughly.

The course of the second stage in the synthesis is heavily dependent on the temperature at which the process is run. At 973 or 993 K, the reaction mixtures kept in the furnace for 120 or 30 min, respectively, finally contain a minute amount of $Fe_8V_{10}W_{16}O_{85}$. Gradually, the amount of $Fe_8V_{10}W_{16}O_{85}$ in the reaction mixture increases markedly as the amount of WO_3 decreases. At the same time, the gradual fading of the $FeVO_4$ diffraction lines can be observed.

When the synthesis is carried out at 1013 K, just after stage I has terminated, both $Fe_8V_{10}W_{16}O_{85}$ and unidentified phase X appear while $FeVO_4$ is still present in the reaction mixture. The amount of WO_3 diminishes at the same time. As the reaction proceeds, the $Fe_8V_{10}W_{16}O_{85}$ content increases rapidly, while the amount of

phase X, after reaching a maximum in the 4 h process, starts to decrease. The progress of the reaction decreases noticeably when $FeVO_4$ has disappeared. When the synthesis is carried out at 1033 K, the unidentified phase X appears in the reaction mixture after the first stage of the process has finished. Its amount increases rapidly and is much larger than when the process is carried out at 1013 K. The amount of phase X reaches a maximum after 60 min and subsequently decreases. However, after 45 min, $Fe_8V_{10}W_{16}O_{85}$ can be observed and its content increases considerably with time.

In order to confirm the results of X-ray phase analysis, two samples were additionally examined by IR spectroscopy. The samples selected were those heated at 1013 K for 30 and 180 min.

Figure 1 shows the IR spectra of the selected samples, compared with the IR spectra of the initial oxide mixture (curve a) and the pure $Fe_8V_{10}W_{16}O_{85}$ phase (curve d). The IR spectrum of the $Fe_8V_{10}W_{16}O_{85}$ includes broad bands with maxima at 920, 665, 514, 490, 372 and 324 cm^{-1}. The IR spectrum of the initial oxide mixture (curve a) contains a narrow absorption band with maximum at 1024 cm^{-1}, attributable to V_2O_5 [4]. It is the only selective band brought about by V_2O_5. On the other hand, a broad absorption band within the frequency range 950–650 cm^{-1}, with maxima at 848 and 776 cm^{-1} and a shoulder at 934 cm^{-1}, is produced by WO_3 [5]. Two other broad and not very intensive bands, with maxima at ~600 and 488 cm^{-1}, characterize both V_2O_5 and Fe_2O_3 [4, 6]. Finally, an absorption band with maximum at 370 cm^{-1} is jointly characteristic of all oxides present, i.e. V_2O_5, Fe_2O_3 and WO_3 [4–6].

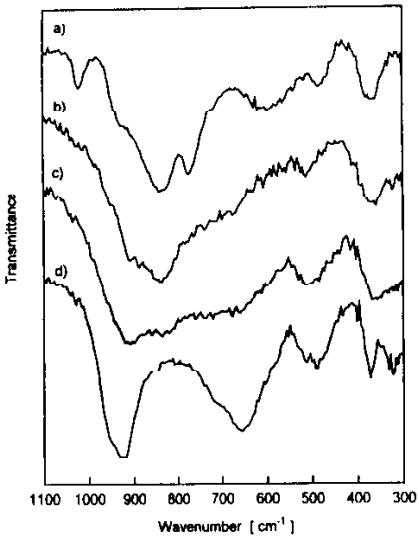

Fig. 1 IR spectra of a – initial mixture of Fe_2O_3, V_2O_5 and WO_3; b – sample heated for 30 min at 1013 K; c – sample heated for 180 min at 1013 K; d – pure $Fe_8V_{10}W_{16}O_{85}$

X-ray phase diffraction of a sample heated at 1013 K for 30 min demonstrates that it contains considerable amount of WO_3 and $FeVO_4$, and traces of $Fe_8V_{10}W_{16}O_{85}$ and an unidentified phase X. The sample does not contain V_2O_5. The IR spectrum of the sample prepared under these conditions (Fig. 1 curve b) does not contain the 1024 cm^{-1} absorption band characteristic of V_2O_5. Instead, there are bands at 910, 670 and 510 cm^{-1}, characteristic of $FeVO_4$ [7]. Thus, it can be concluded that V_2O_5 can react with Fe_2O_3 to completion, giving $FeVO_4$.

X-ray phase analysis of sample 2, heated at 1013 K for 180 min shows a large amount of $Fe_8V_{10}W_{16}O_{85}$, minute quantities of phase X and traces of $FeVO_4$. At the same time, the diffraction line intensity characteristic of WO_3 is decreased considerably. The IR spectrum of the sample reveals considerable increases in intensity of bands with maxima at 920, 665 and 514 cm^{-1}, characteristic of $Fe_8V_{10}W_{16}O_{85}$. The absorption band with maximum at 845 cm^{-1}, distinctive of WO_3 [5], is noticebly decreased.

Thus, the results of X-ray phase analysis are confirmed by IR spectroscopy. Analysis of the diffraction patterns of samples heated at 1013 and 1033 K, i.e. those containing the unidentified phase X, indicated that phase X can be distinguished by the following diffraction reflections, d [nm]: 0.504, 0.3958, 0.3361, 0.2798, 0.2521 and 0.2378. Attempts to identify phase X and to prepare it in a pure state have proved unsuccessful so far. However, analysis of the intensities of the diffraction lines in the diffraction patterns for samples containing maximal amounts of phase X demonstrates that WO_3 is involved in the formation of the compound to a very small extent. In contrast, the appearance of $Fe_8V_{10}W_{16}O_{85}$ in the reaction mixture is associated with a considerable decrease in intensity of the diffraction lines characteristic of WO_3.

The presence of a liquid phase in small amounts in the reaction mixture can be observed in the process of sintering of most of the solid materials. If the liquid phase wets the grains sufficiently and is capable of dissolving large amounts of a solid phase, the sintering process will be accelerated considerably [8]. Therefore, the synthesis of $Fe_8V_{10}W_{16}O_{85}$ proceeds at a high reaction rate observable at as low a temperature as 973 K, while at up to 923 K the final product is not produced even after a very long period of time [2].

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