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INVESTIGATION OF THERMAL DECOMPOSITION OF CrO_x ($x \geq 2.4$)

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Abstract

The phase transitions and thermal effects occurring during annealing in air of material with general formula CrO_x ($x \geq 2.4$) have been investigated. The investigations were performed with TG, DTA, DSC, EGA, XRD and other spectral techniques. The formation of an amorphous phase with average composition Cr_5O_{12} in the range 300–400°C has been observed. Further heating leads to partial loss of oxygen, simultaneous decay of Cr_2O_5 and CrO_2 phases and formation of nonstoichiometric Cr_2O_{3+x}. The distinct loss of mass is observed in the range 415–428°C, connected with evolving oxygen and small amount of nitric oxides. Thermal effects accompanying the mass changes depend on the mass of the sample. When the mass decreases, the transition from exothermic to endothermic effects is observed. This phenomenon can be explained as the competition between two processes: reconstruction of the crystalline lattice (endothermic effect) and recombination of the evolved atomic oxygen (exothermic effect).

Keywords: chromium nitrate nonahydrate, chromium oxides, phase transition, thermal decomposition

Introduction

Chromium forms several oxides and oxide hydrates from which the most known and important are chromium(VI) oxide CrO_3, chromium(III) oxide Cr_2O_3 and hydrated chromium dioxide $CrO_2 \cdot nH_2O$. In addition, among them there are many intermediate products with complex structures and properties, which depend on temperature, gaseous atmosphere, composition, humidity, pressure, etc. [1–3]. The superior properties of supported chromium oxide catalyst in alkane dehydrogenation are well-known, and $CrO_x/Al_2O_3(SiO_2, ZrO_2)$ catalysts are widely used as the commercial one [4, 5]. Chromium(III) oxide is an important refractory material because of its high melting point (about 2300°C) and high-temperature oxidation resistance. As Cr_2O_3 shows poor sinterability, only reactive powders for this purpose can be applicable [6, 7]. Ultrafine Cr_2O_3 powders have a wide range of applications including green pigments, coating materials for thermal protection and wear resistance [8, 9]. Ther-

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mal decomposition of Cr-salts such as chromium(III) nitrate nonahydrate (CNN) is a common preparation method for Cr_2O_3 and many other chromium compounds [7, 9–12, 15]. Depending on heating rate, final annealing temperature, type of gas atmosphere (inert, oxidising or reducing) etc., decomposition of this salt leads to different intermediate products with different physical properties and chemical composition. These conditions have also important influence on many properties of final decomposition products [7, 9–11, 13–15]. The products of the thermal decomposition of CNN obtained below 250°C are hygroscopic and therefore the investigation of their structure and properties is complicated [16–19].

Figure 1 presents TG and DTA curves of CNN heated with a rate of 5°C min^{-1} in flowing synthetic air atmosphere. The EGA for oxygen and nitric oxide were performed with the same rate of heating in pure helium atmosphere [19]. The TG curve between 300–400°C shows that the mass of decomposed sample is practically constant. The average mass loss of the initial CNN samples in this temperature range is 0.3% (22.8–23.1%). On the other hand, the Cr(VI) content of the samples between 260–310°C is in the range 7.6–8.2% which points to a molar ratio of $Cr^{6+}/Cr^{3+}\approx1.5$, which is in agreement with total formula $Cr_2(CrO_4)_3\equiv Cr_5O_{12}$ [17, 18].

During heating the CNN sample dissolves in its hydration water at about 50°C (Fig. 1 – the first endothermic peak on DTA curve). Further heating causes gradual loss of water with simultaneous decomposition and liberation of gaseous products. The decomposition products have the form of tight spheres, in which residual gaseous products can be trapped [20, 21]. These phenomena lead to considerable enlargement of the product volume with respect to the initial sample and the thermal contact between the sample and crucible becomes poor. As a consequence, the DTA curve, particularly at its final part (410–430°C) can be indistinct and difficult for interpretation. It is possible to avoid this phenomenon by using under investigation

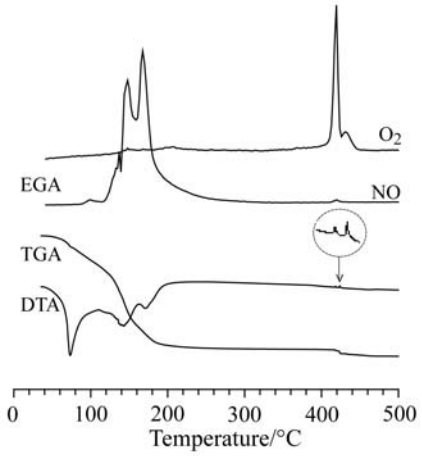

Fig. 1 TG and DTA curves obtained by heating of $Cr(NO_3)_3\cdot9H_2O$ at 5°C min^{-1} in synthetic air flow. The QMS analyses of selected gaseous product (O_2, NO) were performed in the stream of helium

some partially decomposed, not hygroscopic samples. Based on known investigation results [16, 17] it was stated that the best way was to employ the CNN decomposition product obtained at about 300°C. Samples collected at this temperature are stable and have a well-known chemical composition. They can be easily homogenized and ground to destruct their spherical structure. In addition, the mass of these samples receives about 23% of initial mass of the CNN. This fact allow to increase mass of decomposed samples for DTA/DSC (about 5x regarding to CNN) and precisely investigated thermal effects of the final stage of thermal decomposition.

The thermal effects and phase transitions occurred during heating for partially decomposed $Cr(NO_3)_3 \cdot 9H_2O$ samples obtained at 300°C, in air, have been investigated in the present work.

Experimental

Materials

Chromium nitrate nonahydrate, $Cr(NO_3)_3\ \ 9H_2O$ was used for preparation as initial compound. NaOH and $K_2Cr_2O_7$ were used for the spectral analysis. All reagents were analytical grade (POCh, Gliwice, Poland). The samples used for investigations were obtained from portion of CNN samples, in size of 0.47±0.03 g. The CNN samples were placed on a platinum plate and heated up to 300°C with a rate of 5°C min^{-1} in air. The volume of the furnace chamber was 100 cm^3 and the airflow was 100 cm^3 min^{-1} (controlled by flowmeter), which corresponds to 60 times per h of the atmosphere exchange. The decomposition process was programmed and controlled by computer. The flow of the synthetic dry air enables a quick removal of gaseous decomposition products such as water vapor and nitric oxides. The small portions of partially decomposed CNN samples were collected, carefully homogenized, ground and stored in the desiccator over anhydrous $CaCl_2$.

Thermal and mass spectroscopy (EGA) analyses

The solid samples were analyzed using a SDT 2960 simultaneous DTA-TG and DSC 2010 apparatus (TA Instrument, USA) as well as EGA (Evolved Gas Analysis) by QMS (Balzers Instrument, Switzerland). The mass of the sample for TG/DTA investigations does not exceed 50 mg and for DSC – 15 mg. Both investigations were performed in synthetic airflow atmosphere with a heating rate of 5°C min^{-1}. The EGA investigation was realized in spectrally pure helium atmosphere.

X-ray diffractometry

X-ray powder diffractometry (XRD) was carried out with the XRD7 Seifert diffractometer with Ni-filtered CuK_α. The diffractometer was operated with steps of 0.01° and a counting time of 10 s. Continuous intensity trace as a function of 2Θ was recorded. The obtained diffractograms were compared with ASTM standards to identify the phases.

Spectral analysis

The samples of the decomposed CNN used to analyze the Cr(VI) content were obtained using a modified Paulik–Paulik–Erdey derivatograph (MOM, Hungary). Preparation and procedure were identical with those described in the preceding chapter. After the temperature set point was achieved, the heater was automatically stopped. The sample was then dissolved in 20 cm^3 of 20% NaOH and quantitatively transferred to a 100 cm^3 graduated flask.

The samples prepared for investigation of Cr(VI) content were analyzed by means of the spectral method using an UV/VIS Philips spectrometer Model PU 8750 (England). 10 cm^3 of the alkaline solution were transferred to another 100 cm^3 graduated flask which was then filled to the scale mark. The solution was next filtrated through dense filter to remove the colloidal suspension of $Cr(OH)_3 \cdot nH_2O$. The calibration curve was prepared using aqueous solution containing adequate amounts of $K_2Cr_2O_7$. The filtrates were analyzed using the wavenumbers 366 and 400 cm^{-1}.

Results and discussion

As shown in Fig. 1, heating of the sample in the range from 300 to about 415°C causes only little changes in mass. Above this temperature, in the range 415–430°C, a distinct loss of mass takes place. It is accompanied by evolving of oxygen and formation of the nonstoichiometric Cr_2O_{3+x} phase. In addition, EGA investigation [19] at this temperature range shows a small amount of nitric oxides (NO, NO_2). These phenomena can be explained as thermal internal decomposition of solids [20, 21], connected with the reconstruction of their internal structure. Oxygen and chemisorbed (or trapped) nitric oxides are liberated during these processes. Further heating causes a gradual mass loss related to evolving of residual excess of oxygen ($x \rightarrow 0$), related mostly to decomposition of Cr_2O_5 and CrO_2 phases and formation of stoichiometric chromium(III) oxide.

The quantitative analysis of chromium(VI) content in samples obtained during heating CNN in the temperature range of 260–310°C, shows that it decreases from 8.2 to 7.6±0.1%. Based on these results and on the assumption that the residue after decomposition consists of chromium(III) and chromium(VI) oxides mixtures, two limiting compositions: $Cr_5O_{12.2}$ and $Cr_5O_{11.9}$ can be calculated. For simplicity it was assumed that the oxide mixture obtained during heating CNN in air up to 300°C may be described by the general formula Cr_5O_{12}.

As it is revealed by Fig. 1, further heating of this product leads to its decomposition in accordance with the general reaction:

$$2Cr_2(CrO_4)_3 \rightarrow 5Cr_2O_3 + 9/2O_2$$

This process proceeds through several intermediate stages.

Figure 2 illustrates the normalized DTA curves of CNN (a) as well as DTA (b) and DSC curves (c–h) of Cr_5O_{12} samples heated in synthetic air. The masses of investigated samples were: a) 43.99 mg, b) 10.64 mg, c) 10.68 mg, d) 5.178 mg, e) 3.032 mg, f)

2.032 mg, g) 0.778 mg and h) 0.391 mg. Analysis of these results show that decomposition of CNN or Cr_5O_{12} to Cr_2O_3 phase takes place in two main steps.

Figure 2a shows two exothermic DTA effects monitored during decomposition of CNN: the first with maximum at 416°C and the other at 422°C. This is interpreted so far to the thermal effects related to the crystalline formation of α-Cr_2O_3 from amorphous product [16].

Figure 2b presents the DTA curve of Cr_5O_{12}. Both samples have at 410°C practically the same mass, but adequate DTA curves are a little different. The temperature of the first exothermic effect is in good agreement with that of CNN but the other, at 426°C, has a small preceding endothermic effect. The next curves (Fig. 2c–g) were obtained of Cr_5O_{12} samples investigated with a DSC apparatus. The sample represented by Fig. 2c has, in relation to CNN, the same mass as described by 2b. As in Fig. 2b the other exothermic peak is preceded by an endothermic effect.

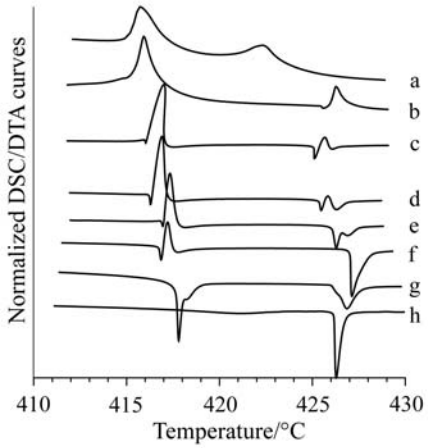

Fig. 2 The normalized curves of a – DTA for CNN; b – DTA for Cr_5O_{12}; c–h – DSC for Cr_5O_{12} samples

It is easy to notice that by moderate decrease of the sample mass the exothermic effects change into an endothermic one (Fig. 2d–g). For the sample with the smallest mass (Fig. 2h) the first peak practically disappeared, while the second is very sharp. These observations do not agree with literature data (only one exothermic effect). The following hypothesis can be formulated: in the range 415–430°C the structure arrangement process proceeds in two endothermic stages. The endothermic processes can be attributed to decomposition of the crystal lattice, their reconstruction and evolving the excess of atomic oxygen. The exothermic effects, which grow with the growth of sample mass, can be explained as recombination of atomic oxygen evolving from the sample. Decreasing of the sample mass increases diffusion of the atomic oxygen to the environment and causes that the exothermic reaction of recombination takes place outside the measurement place.

To confirm above hypothesis that the exothermic effects observed on DTA curves cause by recombination of atomic oxygen evolved during rebuilding of crystalline lattice

the following experiment was done. Samples with different mass of the parent material (CNN calcinated with rate of 5°C min^{-1}, 300°C, air) were heated in DSC apparatus in different atmospheres with rate 5°C min^{-1}. The first part of these samples were placed in aluminum pans and tight covered by adequate lid for simplification of expected atomic oxygen recombination. Decomposition of these samples was done in the air atmosphere. The second part of the samples (in comparable sizes) were placed in open pans and heated in the stream of helium to reduce the partial pressure of oxygen and made recombination process more difficult. Results of these investigations are presented in Fig. 3.

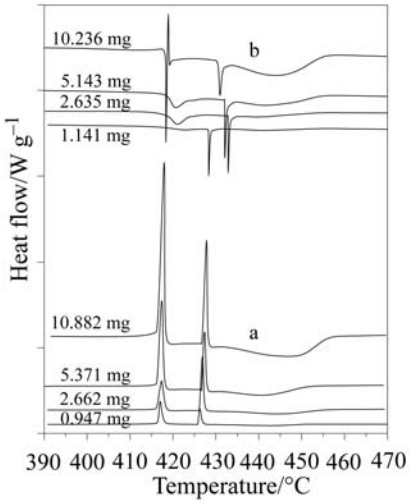

Fig. 3 Curves of Cr_5O_{12} samples heated in different conditions: a – covered pans, air, b – open pans, helium. The distance between ticks on *y*-axis is equal to 10 W g^{-1}

Part marked by (a) represents experimental DSC data for the samples heated in covered pans while part (b) shows analogous results for samples decomposed in open pans. The DSC curves of the samples (a) shows in the range 410–430°C two sharp, exothermic effects and one wide endothermic effect with minimum in the range 440–450°C. For the samples heated in helium (b) we have obtained quite different shapes of DSC curves. For sample with size close to 1 mg there was observed only one distinct endothermic effect (~428°C). Increase of sample size (2.635 and 5.143 mg) leads to appearing two endothermic effects in the range 415–435°C. Further increase sample size cause difficulties in atomic oxygen evolution and made easier recombination in the sample volume. The DSC curve obtained for largest sample (10.236 mg) reveal *vs*. an endothermic effect background the exothermic one.

In order to investigate the influence of temperature on the structural changes of Cr_5O_{12}, X-ray powder diffractograms of samples obtained at 300, 400, 420°C (after first exothermic peak – Fig. 2b), 430°C (after second peak), 500, 600 and 700°C were performed. The examined samples were prepared by heating Cr_5O_{12} in the DTA/TG equipment in air with a rate of 5°C min^{-1}. Results of these investigations are presented in Fig. 4.

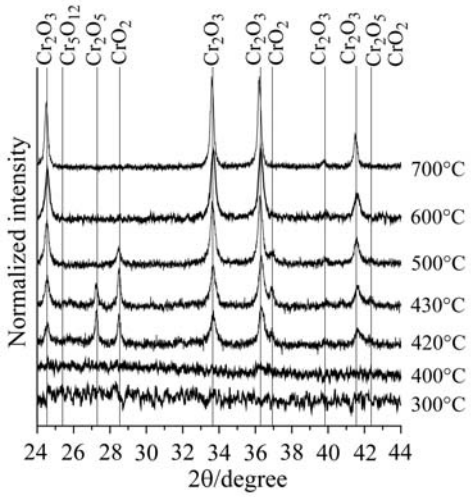

Fig. 4 XRD patterns of Cr_5O_{12} samples heated to the different temperatures in air

XRD patterns show that the initial sample (CNN heated up to 300°C) as well as the sample from 400°C are completely amorphous. Taking into account the analytical results, the sample can be formally described by the hypothetical formula Cr_5O_{12}. However, on the X-ray diffractogram (Fig. 4) no crystalline Cr_5O_{12} phase were observed. The diffraction patterns for samples obtained at temperatures of 420 and 430°C display peaks belonging to Cr_2O_5, CrO_2 and CrO_3. At 500 and 600°C two phases were observed: Cr_2O_3 and CrO_2 (traces). The diffractogram for sample obtained at 700°C show α-Cr_2O_3 only. Obtained results are in good agreement with results, reported by Maciejewski *et al*. [10].

Conclusions

- Thermal decomposition of the CNN in dry air atmosphere leads to the formation of different oxides with variable contents of chromium(VI). The maximum concentrations of the Cr(VI) appear in temperature range of 260–310°C. It can be stated that there exist oxide mixtures, which can be described by the formula Cr_5O_{12}.
- Thermal decomposition above 420°C of the amorphous oxide mixtures with general formula Cr_5O_{12}, causes the formation of crystalline phases: Cr_2O_5, CrO_2 and Cr_2O_3. When the final temperature increases, the amount of Cr_2O_5 and CrO_2 gradually decay. At 700°C only individual crystallites of -Cr_2O_3 remain.
- Phase transformations in the temperature range 415–428°C proceed in two stages. Both stages are connected with two main competitive effects: lattice reconstruction (endothermic) and atomic oxygen recombination (exothermic).
- The liberation of nitric oxide over 400°C can be explained as breaking of the CrO_x framework in which NO_x were chemisorbed or trapped.

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