Formation of Chromia from Amorphous Chromium Hydroxide

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Forced hydrolysis of Cr(NO₃)₃ in a solution of decomposing urea was investigated. Chromium hydroxide precipitates were amorphous for the final pH values up to ~9 to 9.5. Heating of amorphous chromium hydroxide up to 360 °C produced Cr₂O₃ crystallites of the order of 20 nm, whereas after heating up to 825 °C the crystallite size of Cr₂O₃ increased to the order of 100 nm. Crystallization of Cr₂O₃ was also monitored by FT-IR spectroscopy. TGA/DTA curves, recorded in air, showed thermal behavior of amorphous chromium hydroxides that differed depending on the experimental conditions of their preparation. A sharp exothermic peak between 410 and 420 °C was recorded due to the crystallization of Cr₂O₃. This peak shifted to 600 °C when the heating of amorphous chromium hydroxide was performed in an argon atmosphere. Accelerated crystallization of Cr₂O₃ from amorphous chromium hydroxide in air is explained by the catalytic effect of the higher oxidation states of chromium species, which were probably restricted to the surface of the particles. It is suggested that higher oxidation states of chromium were not stable and they converted to the initial Cr(III) state. XRD did not detect any oxide phase of chromium except for Cr₂O₃.

Key words: chromia, amorphous chromium hydroxide, crystallization, FT-IR spectroscopy, X-ray powder diffraction

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INTRODUCTION

Chromium oxides (Cr$_2$O$_3$, CrO$_2$, CrO$_3$) and oxyhydroxide (CrOOH) have been extensively investigated from different standpoints. Possible industrial applications of these compounds depend on their chemical, physical and microstructure properties. Generally, the properties of these compounds can be modified by synthesis conditions. For this reason, in many investigations, researchers have tried to establish the relation between the properties of chromium oxides and synthesis conditions. Special attention was focussed on the formation and properties of chromia (Cr$_2$O$_3$), which have found important application in high-temperature resistant materials, solar energy collectors, liquid crystal displays, catalysts, etc. Cr$_2$O$_3$ was also detected in the rust formed by corrosion of Cr-containing steels. In this introduction, we shall focus attention on selected works in the literature dealing with chromium hydroxide (Cr(OH)$_3$) and Cr$_2$O$_3$.

Colloidal Cr(OH)$_3$ particles of narrow size distribution were prepared by heating diluted KCr(SO$_4$)$_2$ solution. The basic chromium sulfate polymer served as precursor or heteronucleating agent in the precipitation of the Cr(OH)$_3$ colloids. The possible chemical reactions involved in the precipitation of the Cr(OH)$_3$ colloids were discussed. Surface properties of the Cr(OH)$_3$ were investigated in dependence on the time of heating of KCr(SO$_4$)$_2$ solution (4 · 10$^{-4}$ mol dm$^{-3}$) at elevated temperature. Sulfate ions had a chief role in the process of Cr$^{3+}$ hydrolysis. The surface properties of amorphous Cr$_2$O$_3$ particles and the thermal decomposition products of the starting material were also investigated using acid-base potentiometric titrations. Specific adsorption of sulfates on the particles was observed. Specifically adsorbed sulfates could be desorbed by alkaline washing, but not by acidic washing. Siddiq et al. observed that the surface area of chromium hydroxide gels strongly decreased with an increase of the precipitation pH from ~5 to ~11. This effect was explained by the nature of the chromium hydroxide gel, which is more polymeric at low pH and crystalline at pH > 10.

Chromium hydroxide gel was precipitated from Cr(NO$_3$)$_3$ solution adding hydrazine monohydrate. Crystallization of Cr$_2$O$_3$ was observed at 380 to 405 °C. The lattice parameters of Cr$_2$O$_3$ (in terms of hexagonal axes), prepared by heating the gel at 450 °C for 1 h, were $a = 0.4955$ nm and $c = 1.359$ nm, the space group being $Rar{3}c$. Cr$_2$O$_3$ pellets having 98.9% of theoretical density were produced by hot isostatic pressing at 1100 °C for 2 h and 196 MPa. Hou et al. dissolved Cr(NO$_3$)$_3$ · 9H$_2$O in water and, after heating the solution to dryness, the solid residue was sintered and heated up to 1000 °C. Less than 1% CrO$_2$ was estimated in all samples. The samples obtained after heating at 400 to 600 °C showed phases with crystallite size of 17 to 25 nm, respectively. Thin Cr$_2$O$_3$ films were prepared by the CVD method using chromium acetylacetonate and chromium hexacarbonyl. In the case of
chromium hexacarbonyl, the reaction temperature could be decreased from 150 to 60 °C by irradiation with UV light.

Maciejewski et al.\textsuperscript{10} investigated the thermal decomposition of the Cr(NO$_3$)$_3$\cdot 9H$_2$O salt and observed the formation of CrO$_2$ as a stable phase. The ratio of CrO$_2$ to Cr$_2$O$_3$ depended on the heating conditions of the starting salt. For complete phase transformation to Cr$_2$O$_3$, a temperature higher than 600 °C was required. Rapid crystallization of the amorphous intermediary, obtained at lower temperatures, produced Cr$_2$O$_3$ as a single phase at ~380 °C. The phase transformation CrO$_2$ $\rightarrow$ CrOOH (yield ~95%) and the reversibility of this phase transformation were observed under specific experimental conditions.

In a research into chromium oxides, significant attention was paid to the characterization of chromium oxides supported on various oxide carriers. SiO$_2$ and γ-Al$_2$O$_3$ were impregnated\textsuperscript{11} with the Cr(NO$_3$)$_3$\cdot 9H$_2$O salt, Cr$_2$O$_3$\cdot 5H$_2$O gel or CrO$_3$ and then the oxides were heated at 600 °C for 5 h. The Cr$_2$O$_3$ particles on SiO$_2$ were predominant, while dispersed chromates were observed on γ-Al$_2$O$_3$, irrespective of the type of the precursor used. Differences in the composition of coatings were explained by differences in the surface chemistry and population of terminal OH groups on the adsorbents. Vuurman et al.\textsuperscript{12} also found differences in the chromium oxide coatings on SiO$_2$ adsorbent, on one the hand, and on Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ adsorbents, on the other. Diffuse reflectance spectroscopy\textsuperscript{13} and Raman spectroscopy\textsuperscript{14} were used to investigate the oxidation state of chromium and the nature of the chromium-oxygen bond. TiO$_2$ particles were impregnated\textsuperscript{15} with Cr(NO$_3$)$_3$\cdot 9H$_2$O and then heated under different conditions. X-ray absorption near edge structure (XANES) of the samples indicated Cr$_2$O$_3$ and CrO$_2$ in the coatings, whereas the presence of chromates and/or CrOOH was not confirmed. Baiker et al.\textsuperscript{16–20} systematically investigated chromium oxide coatings on TiO$_2$ adsorbent. This catalyst is important in the selective catalytic reduction (SCR) of nitric oxide (NO) with ammonia in the presence of an excess of oxygen. Amorphous chromia was found to be more active and selective to N$_2$ formation than crystalline chromia. Musić et al.\textsuperscript{21,22} investigated the Cr$_2$O$_3$–Fe$_2$O$_3$ system using XRD and spectroscopic techniques. Rousset and Pâris\textsuperscript{23} also investigated the formation of solid solutions in the Cr$_2$O$_3$–Fe$_2$O$_3$ system.

In the present work, we focus on the forced hydrolysis of a solution of Cr(NO$_3$)$_3$ and urea. Selected samples of amorphous chromium hydroxides, obtained as hydrolytic products, were subjected to thermal treatment in order to ascertain the conditions of the phase conversion of amorphous Cr(OH)$_3$ to the oxide phase. The results of the present investigation are important for engineers involved in the production of thin chromium oxide films or catalysts.
EXPERIMENTAL

The Cr(NO$_3$)$_3$·9H$_2$O salt and urea of analytical purity were used. The solutions were prepared using doubly distilled water. Hydrolysis experiments were performed using an oil bath (± 1 °C) with reflux. For long period of times (1 day and more) the precipitation systems were aged under autoclaving conditions. After an appropriate aging time, the suspensions were centrifuged to separate the precipitate from mother liquor. An ultra-speed centrifuge, Sorvall RC2-B, with an operational range up to 20000 r.p.m. was used. Precipitates were subsequently washed with doubly distilled water and dried. The history of selected samples is given in Table I. Commercial Cr$_2$O$_3$ (purity 99.999%) supplied by Ventron was also used.

The pH of the mother liquor was measured using a pH-meter, model pHM–26, manufactured by Radiometer. A combined glass/calomel electrode with an operational range up to pH 14, also manufactured by Radiometer, was used.

X-ray powder diffraction (XRD) patterns were taken using an automatic Philips diffractometer, model MPD 1880 (CuK$_\alpha$ radiation, graphite monochromator, proportional counter). From the broadening of the diffraction lines of Cr$_2$O$_3$, the crystallite sizes were estimated using the Scherrer equation

$$D = \frac{0.9 \lambda}{\beta \cdot \cos \theta}$$

where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle and $\beta$ is the pure full width of the diffraction line at half the maximum intensity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental conditions</th>
</tr>
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<tbody>
<tr>
<td>C1</td>
<td>Hydrolysis of the solution 0.1 M Cr(NO$_3$)$<em>3$ and 0.5 M urea at 100 °C for 9 h. $\text{pH}</em>{\text{final}} = 7.05$</td>
</tr>
<tr>
<td>C2</td>
<td>Sample C1 was heated in air up to 240 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C3</td>
<td>Sample C1 was heated in air up to 290 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C4</td>
<td>Sample C1 was heated in air up to 360 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C5</td>
<td>Sample C1 was heated in air up to 825 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C6</td>
<td>Hydrolysis of the solution 0.1 M Cr(NO$_3$)$<em>3$ and 1.0 M urea at 100 °C for 9 h. $\text{pH}</em>{\text{final}} = 8.07$</td>
</tr>
<tr>
<td>C7</td>
<td>Sample C6 was heated in air up to 825 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C8</td>
<td>Hydrolysis of the solution 0.1 M Cr(NO$_3$)$<em>3$ and 2.0 M urea at 100 °C for 9 h. $\text{pH}</em>{\text{final}} = 8.92$</td>
</tr>
<tr>
<td>C9</td>
<td>Sample C8 was heated in air up to 825 °C at the rate 10 °C/min</td>
</tr>
<tr>
<td>C10</td>
<td>Hydrolysis of the solution 0.1 M Cr(NO$_3$)$<em>3$ and 0.3 M urea at 90 °C for 3 days. $\text{pH}</em>{\text{final}} = 8.37$</td>
</tr>
<tr>
<td>C11</td>
<td>Sample C10 was heated in argon up to 650 °C at the rate 10 °C/min and then cooled also in argon</td>
</tr>
</tbody>
</table>
The FT-IR spectra were recorded using a Perkin-Elmer spectrometer (model 2000). The spectra were processed using the Infrared Data Manager (IRDM) program also supplied by Perkin-Elmer. The specimens were pressed into KBr matrix.

Thermal analysis was performed using an instrument produced by Netzsch. The temperature was controlled by a Pt-PtRh(10%) thermocouple, and the heating rate was 10 °C min⁻¹. TGA/DTA instrumentation was also used for the heating of amorphous chromium hydroxide under controlled conditions to obtain thermal decomposition products for further instrumental characterization.

RESULTS AND DISCUSSION

In aqueous medium, urea undergoes hydrolysis at elevated temperatures in accord with the chemical reaction:

$$(\text{NH}_2)_2\text{CO} + 3 \text{H}_2\text{O} \rightarrow 2 \text{NH}_4^+ + 2 \text{OH}^- + \text{CO}_2$$

Increase of the pH-value in a solution of decomposing urea depends on the initial concentration of urea, temperature and time of heating. Figure 1 illustrates the dependence of pH on time during the forced hydrolysis of Cr(NO₃)₃ solution in decomposing urea in autoclaving conditions. In the presence of decomposing urea, a significant pH-increase under control conditions can be achieved, and in the present work this effect was used to accelerate the hydrolysis of Cr³⁺ ions for the precipitation of the hydroxide phase. The analysis of the precipitates showed their amorphous character, even for the precipitates obtained at relatively high pH values (pH ~9 to 9.5) and for long times of aging, up to 60 days.

![Figure 1](image)

Figure 1. Dependence of pH on the time of the forced hydrolysis at 90 °C of 0.1 M Cr(NO₃)₃ solution with varying initial concentrations of urea.
Figure 2 shows characteristic parts of the X-ray powder diffraction patterns of sample C1 and its thermal decomposition products (samples C4 and C5). Diffraction patterns were recorded at room temperature.

Figure 2 shows characteristic parts of the X-ray powder diffraction patterns of amorphous chromium hydroxide (sample C1) and its thermal decomposition products. It can be seen that sample C1 is completely amorphous. After the heating of sample C1 up to 290 °C, the thermal decomposing product was amorphous, as proved by XRD. With an increase of the heating temperature up to 360 °C, crystalline Cr$_2$O$_3$ appeared as well as an amorphous fraction (sample C4). On the basis of the broadening of diffraction lines, it was estimated that the crystallite size of Cr$_2$O$_3$ (sample C4) was of the order of 20 nm. In nanotechnology, it is generally assumed that particles up to ~30 nm belong to the so-called nanosized range. We note that particle size differs from crystallite size by definition; however, in the case of very small particles their size is often comparable with the crystallite size, as estimated by the Scherrer formula. After
heating sample C1 up to 825 °C (sample C5), crystalline Cr₂O₃ was detected with slightly broadened X-ray powder diffraction lines. The crystallite size of Cr₂O₃ in sample C5 and those estimated for the samples obtained by heating other chromium hydroxide precipitates up to 825 °C were of the order of 100 nm. Also, the crystallite shape of samples C4 and C5 was a little asymmetric, thus showing a smaller dimension along the c-axis.

Figure 3 shows the FT-IR spectra of amorphous chromium hydroxide (sample C1) and its thermal decomposition products (samples C2, C3, C4 and C5). The spectra were recorded at room temperature.

heating sample C1 up to 825 °C (sample C5), crystalline Cr₂O₃ was detected with slightly broadened X-ray powder diffraction lines. The crystallite size of Cr₂O₃ in sample C5 and those estimated for the samples obtained by heating other chromium hydroxide precipitates up to 825 °C were of the order of 100 nm. Also, the crystallite shape of samples C4 and C5 was a little asymmetric, thus showing a smaller dimension along the c-axis.

Figure 3 shows the FT-IR spectra of sample C1 and its thermal decomposition products (samples C2 to C5). Sample C1 was characterized by a very broad band centered at 523 cm⁻¹. A similar spectrum was also recorded for sample C2. In the spectrum of sample C3, a very broad IR band was centered at 533 cm⁻¹. A weak shoulder at 633 cm⁻¹ and a weak band at 438 cm⁻¹ are visible, indicating a certain level of structural ordering in the amorphous phase. The IR bands characteristic of Cr₂O₃ were visible in the spectrum of sample C4 and they were well developed in the spectrum of sample C5. Figure 4 shows FI-IR spectra of samples C7 and C9 with the bands typical of Cr₂O₃, and the spectrum of commercial Cr₂O₃ (purity 99.999%). The FT-IR spectra of samples C5, C7, C9 and commercial Cr₂O₃
show relative differences in the intensities of the shoulders at 656 and 619 cm$^{-1}$. Commercial Cr$_2$O$_3$ also showed a shoulder at 537 cm$^{-1}$. These differences can be related to the differences in crystallinity, particle size and shape of the Cr$_2$O$_3$ samples.

The IR spectrum of Cr$_2$O$_3$ was investigated by several researchers and, here, only selected works will be reviewed. Renneke and Lynch$^{24}$ investigated the IR modes of Cr$_2$O$_3$ using a classical oscillator analysis of its reflectivity data. The modes vibrating parallel to the c-axis occurred at 538 and 613 cm$^{-1}$, whereas the modes vibrating perpendicular to the c-axis occurred at 417, 444, 532 and 613 cm$^{-1}$. Serna et al.$^{25}$ recorded IR spectra for Cr$_2$O$_3$ having dominantly lath-type particles. Small contributions of cylinder- or sphere-type particles were related to the broad shoulder at 650 to 700 cm$^{-1}$. For the dominant morphology, the bands at 617, 556, 443 and 305 cm$^{-1}$ were ascribed to $E_u$ modes, whereas the bands at 415 and approximately 720 cm$^{-1}$ were ascribed to $A_{2u}$ modes. The characteristic IR bands were used to identify the Cr$_2$O$_3$ phase in the rust formed by the high-temperature corrosion of the alloy Inconel 718.$^{26}$ IR spectroscopy was also applied in the investigations$^{27-29}$ of Cr$_2$O$_3$ surface chemistry.
Figure 5 shows TGA/DTA curves of amorphous chromium hydroxide (samples C1, C6 and C8) obtained in air. In spite of the fact that all these samples were amorphous, the DTA curves indicated that their thermal behavior differed depending on the hydrolysis conditions, i.e. the initial concentration of urea. Sample C1 showed a broad endothermic peak centered at 200 °C and intersected by two exothermic peaks at 265 and 325 °C. A sharp exothermic peak corresponding to Cr₂O₃ crystallization was positioned at 410 °C. XRD analysis showed that Cr₂O₃ crystallization started at lower temperatures (Figure 2, sample C4). The DTA curve of sample C6 showed a shoulder at 285 °C, whereas the DTA curve of sample C8 showed a shoulder at 290 °C. The second exothermic peak shifted from 325 to 340 °C in the order C1→C6→C8.

Carruthers et al. heated chromium oxide gel in an oxygen atmosphere and observed exothermic peaks at 230 and 280 °C and a sharp exothermic peak at 400 °C. Heating in nitrogen atmosphere shifted the Cr₂O₃ crystallization peak from 400 to 580 °C. It was concluded that the crystallization of
Cr$_2$O$_3$ at lower temperatures in an oxygen atmosphere was promoted by a fast oxidation reaction Cr(III)→Cr(VI). Measurements of the surface area (B.E.T.) of the thermal decomposition products of chromium oxide gel in air, vacuum or dry nitrogen$^{31}$ showed a shift of maximum surface area to ~400 °C in the case of nitrogen atmosphere. It was also concluded that the exothermic peak at ~230 °C is due to the formation of orthorhombic CrOOH. Ratnasamy and Léonard$^{32}$ neutralized 0.1 M Cr(NO$_3$)$_3$ solution with NH$_4$OH solution up to pH 10.5. The authors reported that the precipitated chromium hydroxide possessed a crystalline structure. Water molecules were eliminated from the hydroxide precursor below 200 °C and crystalline Cr$_2$O$_3$ was produced at 400 °C. It was also concluded that samples produced up to 240 °C have a »short-range structure« similar to that in HCrO$_2$. Klissurski and Bluskov$^{33}$ neutralized Cr(NO$_3$)$_3$ solution with NH$_4$OH solution at pH 7 to 8. The authors suggested surface formation of HCrO$_2$ during the heating of chromium hydroxide at lower temperatures. The exothermic peak, due to Cr$_2$O$_3$ crystallization was observed at 380 °C for humid air and at 400 °C for dry air. Giovanoli and Stadelmann$^{34}$ detected only Cr$_2$O$_3$ during thermal decomposition of crystalline Cr(OH)$_3$·3H$_2$O. By decomposition of crystalline Cr(OH)$_3$·3H$_2$O under water vapor, a short range order developed up to 300 °C, which may be attributed to very fine crystallites of CrOOH.

In order to investigate the influence of the atmosphere on the heating of amorphous chromium hydroxide, as prepared in the present work, we performed the experiment in an argon atmosphere. The sample was cooled to room temperature, also in an argon atmosphere, to avoid the possible sample oxidation during the cooling. Figure 6 shows the DTA curve of sample C10 obtained in an argon atmosphere. A strong endothermic peak at 200 °C, due to water loss, was visible. The sharp and very strong exothermic peak shifted to 600 °C. Figure 7 shows FT-IR spectra of amorphous chromium hydroxide (sample C10) and the thermal decomposition product obtained at 650 °C in an argon atmosphere (sample C11). Sample C10 showed a typical FT-IR spectrum of amorphous chromium hydroxide with a very broad band centered at 523 cm$^{-1}$. However, the FT-IR spectrum of sample C11 showed a certain difference in relation to the spectra of Cr$_2$O$_3$ obtained by heating amorphous chromium hydroxide in air. The IR band at 619 cm$^{-1}$ was pronounced and the band at 656 cm$^{-1}$, shown in Figure 4, was strongly suppressed. Also, the relative intensity of the IR band at 412 cm$^{-1}$ was strongly decreased. Precise X-ray powder diffraction (bulk analysis) of sample C11 did not indicate the presence of nonstoichometric Cr$_2$O$_{3-\delta}$ (δ = loss of oxygen) or other oxide phases besides Cr$_2$O$_3$. Another factor that might have influenced the shape of the FT-IR spectrum was the particle size and shape or the sintering effect.$^{25}$ Also, the exothermic shift to 600 °C in the DTA curve,
observed in sample C11, indicated a difference in the chemistry of thermal decomposition in oxidative (air, oxygen) or reductive (nitrogen, argon) atmospheres. It is realistic to suppose that the accelerated crystallization of $\text{Cr}_2\text{O}_3$ from amorphous chromium hydroxide in air involved a catalytic effect of higher oxidation states of chromium. Chromium species were probably restricted to the surface of the particles. However, if they were also present in the bulk, their conversion to the initial Cr(III) state was complete, so that they could not be observed by XRD. Schroeder et al.\textsuperscript{35} monitored in situ thermal dehydration of hydrous chromium hydroxide gel using total electron-yield XAS (X-ray absorption spectroscopy). The authors found that amorphous chromium hydroxide was partially oxidized in argon atmosphere ($\text{Cr(III)} \rightarrow \text{Cr(VI)}$ and possibly $\text{Cr(V)}$). Taking into account the results obtained in the present work, it can be concluded that the chromium oxidation process in an argon atmosphere, as observed by Schroeder et al.,\textsuperscript{35} was not able to catalyze the crystallization of $\text{Cr}_2\text{O}_3$ at lower temperatures, as it was observed in the experiments performed in air atmosphere. For this reason, the sharp exothermic peak of the $\text{Cr}_2\text{O}_3$ crystallization shifted to a significantly higher temperature (600 °C).
The conditions of the forced hydrolysis of a solution of Cr(NO_3)_3 and urea were investigated. In decomposing urea a significant pH-increase could be achieved, thus accelerating the hydrolysis of Cr^{3+} ions. Phase analysis of hydroxide precipitates showed their amorphous character for the final pH values up to ~9 to 9.5 and for long times of aging, up to 60 days.

Heating amorphous chromium hydroxide samples at lower temperature, up to 360 °C, produced Cr_2O_3 crystallites of the order of 20 nm. However, after heating up to 825 °C, the crystallite size of Cr_2O_3 increased to the order of 100 nm. Crystallization from amorphous chromium hydroxide was also monitored by FT-IR spectroscopy. The FT-IR spectra obtained in the present work were compared with the spectrum of commercial Cr_2O_3 (purity 99.999%).

TGA/DTA curves recorded in air showed thermal behavior of the samples that differed depending on the hydrolysis conditions, i.e. the initial concentration of urea. The endothermic peak due to water loss varied between 200 and 235 °C and was intersected by two exothermic peaks at 265 to
290 °C and 325 to 340 °C, respectively. A sharp exothermic peak between 410 and 420 °C, due to the crystallization of Cr₂O₃, was observed.

FT-IR spectrum of Cr₂O₃, produced in argon atmosphere, showed a pronounced IR band at 619 cm⁻¹, a strong suppression of the band at 656 cm⁻¹ and a strong decrease of the relative intensity of the band at 412 cm⁻¹. For the same sample, an exothermic shift to 600 °C in the DTA curve was observed. It was suggested that the accelerated crystallization of Cr₂O₃ from amorphous chromium hydroxide in air involved a catalytic effect of higher oxidation states of chromium species, probably restricted at the surface of particles. In the next step, chromium species of higher oxidation states converted to the initial Cr(III) state. The catalytic effect of higher oxidation states of chromium was not involved during the Cr₂O₃ crystallization from amorphous chromium hydroxide in argon atmosphere, or it was very small, and, for this reason, the sharp exothermic peak of the Cr₂O₃ crystallization shifted to 600 °C.

REFERENCES

SAŽETAK

Nastajanje krom(III) oksida iz amorfog krom(III) hidroksida

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Istraživana je ubrzana hidroliza iona Cr³⁺ u otopini Cr(NO₃)₃ i uree pri 100 i 90 °C. Talozi kromova(III) hidroksida bili su amorfni do pH ≈ 9–9.5 i vremena starenja do 60 dana pri 90 °C. Grijanjem amorfog kromova(III) hidroksida do 360 °C dobiveni su kristali Cr₂O₃ veličine ≈ 20 nm, dok su grijanjem ishodnog materijala do 825 °C dobiveni kristali Cr₂O₃ veličine ≈ 100 nm. Kristalizacija Cr₂O₃ također je motivirana primjenom FT-IR spektroskopije. Krivulje TGA/DTA, snimljene u zraku, pokazale su različito termičko ponašanje amorfog kromova(III) hidroksida u ovisnosti o eksperimentalnim uvjetima. Oštar egzotermni vrh između 410 i 420 °C dobiven je zbog kristalizacije Cr₂O₃. Taj egzotermni vrh pomaknuo se na 600 °C kada je amorfni kromov(III) hidroksid zagrijavan u argonu. Ubrzana kristalizacija Cr₂O₃ iz amorfog kromova(III) hidroksida u zraku objašnjena je katalitičkim efektom spojeva kroma s višim oksidacijskim brojevima. Ti spojevi kroma, vjerovatno ograničeni na površinu čestica, nisu bili stabilni i reducirali su se u početni Cr³⁺. Rentgenske difrakcijske slike praha pokazale su samo nastajanje faze Cr₂O₃.