



The evolution of dehydration and thermal decomposition of nanocrystalline and amorphous chromium hydroxide



Zhonglin Huang^a, Changguo Chen^{a,*}, Jiyun Xie^b, Zengxiang Wang^b

^a College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, PR China

^b Chongqing Minfeng Chemical Co., Ltd., Chongqing, Tongnan 402660, PR China

ARTICLE INFO

Article history:

Received 8 June 2015

Received in revised form 9 February 2016

Accepted 13 February 2016

Available online 16 February 2016

Keywords:

Chromium hydroxide

Dehydration

Thermal decomposition

X-ray diffraction

ABSTRACT

Chromic oxide was synthesized through the dehydration and thermal decomposition of nanocrystalline and amorphous chromium hydroxide. The dehydration of amorphous chromium hydroxide had been researched clearly over the past few decades. Here, we mainly explored the different dehydration process between crystalline and amorphous chromium. The two samples were prepared by a simple one-step precipitation at 5 °C and 25 °C, and characterized using X-ray diffraction and high resolution transmission electron microscopy. The evolution of dehydration and thermal decomposition behaviors of the two samples were measured by derivative thermogravimetry and Fourier transform infrared (FT-IR) spectrometry. The dehydration of nanocrystalline chromium hydroxide occurred at 105 °C, 289 °C, and 409 °C, whereas that of amorphous chromium hydroxide occurred at 70 °C, 289 °C, 406 °C, and 443 °C. At approximately 289 °C, the actual quantity of dehydration was only one water molecule, which was in agreement with the theoretical result (expressed as Cr(OH)₃). The FT-IR absorption bands at 3370 and 1620 cm⁻¹ gradually decreased in intensity with increasing annealing temperature and then finally disappeared at 600 °C to become α-Cr₂O₃.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the modern chromium chemical industry, chromium hydroxide is an important intermediate material. Thermal dehydration of hydrated chromic oxide precursor gel (Cr₂O₃·nH₂O) is commonly employed to obtain chromium oxides [1–5]. Chromic oxide has been widely used in ceramics, coatings, printing, and construction materials because of its excellent performance in anti-corrosion, wear resistance, and chemical resistance. The morphology and particle size of Cr₂O₃ differ depending on the dehydration and thermal decomposition behaviors of chromium hydroxide. Chromium oxide particles formed by nanocrystalline chromium hydroxide present emerald color and fine uniformity. However, the chromium oxide formed by amorphous chromium hydroxide presents blue-green and dull color.

Chromium oxide materials are usually prepared by adding a Cr(NO₃)₃·H₂O solution to an ammonia [6–11] or NaOH solution [12], and by hydrolyzing Cr(NO₃)₃ in an autoclave [13]. Many scholars explored the structural evolution of chromium oxides generated from chromium hydroxide precipitates under heat treat-

ment [6–8,12–14]. The existent forms of Cr(III) highlighted in relevant literature include a crystalline hydrous phase in the form of Cr(OH)₃·3H₂O (Cr₂O₃·9H₂O) [15–17] and an amorphous phase in the form of Cr(OH)₃ or Cr(OH)₃·xH₂O, where x is lower than 3 [18–21]. In a sufficiently alkaline environment or at low temperatures, Cr(III) salt solutions induce the precipitation of hydrogen-bonded Cr(OH)₃(OH)₂ crystalline networks. This compound is stable at room temperature but turns into an amorphous phase upon aging in an aqueous suspension or heating at relatively mild conditions. Some studies also discussed the chromium oxide phase when samples were calcined at different temperatures [22–24]. Charlet and Manceau [25], Fendorf et al. [26], and Rai et al. [19,27] studied the local atomic order of amorphous Cr(III) hydroxide through XANES and EXAFS.

The water molecules loss of the amorphous chromium hydroxide has been clearly recognized, but the research on the dehydration of crystalline chromium hydroxide was rarely. With the temperature increase, the water molecules lose gradually, sample changed into all kinds of chromium oxide forms. So far, the chromium oxide forms have not been studied carefully, and water molecules specific quantity lose are also not clear. The final products of chromium oxide differ in physical and chemical properties depending on the different dehydration methods of the two samples. In the present work, we performed precipitation combined with a heat

* Corresponding author. Fax: +86 65106053.

E-mail addresses: 20121801001c@cqu.edu.cn, cgchen@cqu.edu.cn (C. Chen).

treatment to study nanocrystalline Cr(III) hydroxide and amorphous chromium hydroxide nanomaterials. Then, we discussed the characteristics of dehydration with different coefficients. Finally, the specific amounts of water molecules lost to become various chromium oxide forms were investigated at different temperature ranges.

2. Experimental

2.1. Preparation methods

Analytical-grade chromium nitrate hydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Chengdu, Kelong chemical reagent factory) and sodium hydroxide (NaOH , Chuangdong chemical Co., Ltd., Chongqing) solution were used as precursors to prepare an oxide colloid. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5 g) was dissolved in 100 mL of deionized water, and 2 g of NaOH was dissolved in 250 mL of deionized water. At 5°C and 25°C , a NaOH solution was added at a rate of 1 mL min^{-1} into the ion solution with vigorous stirring to form an oxide colloid. The addition of the NaOH solution was terminated when the pH of the oxide colloid reached 8.5. After constant stirring in air for 0.5 h, the obtained oxide colloid was centrifuged at 13,000 rpm for 10 min and washed thrice with distilled water, twice with acetone, and finally once with ethanol to remove NO_3^- and Na^+ . Samples that formed at 5°C and 25°C were labeled as Sample C and Sample A, respectively. Samples of chromium oxide series were prepared by heating chromium hydroxide gel at different temperatures (200°C , 350°C , 425°C , and 600°C) for 2 h in air. All samples were stored in a desiccator.

2.2. Equipment

The crystal structures of the samples were identified using powder X-ray diffraction (Shimadzu XRD-6000, Cu $K\alpha$ target, $\lambda = 0.15406 \text{ nm}$, tube voltage = 35 kV, current = 30 mA), and high resolution transmission electron microscopy (JEM-2010, Japan). Chromium hydroxide gel decomposition was characterized by thermogravimetry (DTG-60H, Shimadzu, heating rate: 10°C/min , atmosphere: nitrogen, flow rate: 50 mL/min) and Fourier transform infrared (FT-IR) spectroscopy (Nicolet 550II, USA). The other equipment used in the study was as follows: a 78-HW magnetic stirrer, a PHS-3C pH meter, and a HS-4 precision thermostatic bath. The prepared chromium hydroxide gel was separated from the solution by a high-speed centrifuge (LXJ-II, Shanghai Medical Instrument Factory, China).

3. Results and discussion

3.1. XRD pattern and HRTEM images of chromium hydroxide and Cr_2O_3

The XRD spectra of plain nanocrystalline Cr(III) hydroxide (C), amorphous chromium hydroxide (A), and chromium oxide in the 2θ range of $10\text{--}80^\circ$ are shown in Fig. 1. Nanocrystalline Cr(III) hydroxide and chromium oxide reveal a high degree of crystallinity, with a grain size of 61 nm. The pattern could be distinctly indexed to a hexagonal phase with lattice constants $a = 5.288 \text{ \AA}$ and $b = 4.871 \text{ \AA}$ for $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ (PDF No. 16-0817). The structure of this crystalline compound can be described as “anti-bayerite” in comparison with that of bayerite $\text{Al}(\text{OH})_3$ [15]. Fig. 2(C) and (A) are the HRTEM images of nano-crystalline and amorphous chromium hydroxide particles. The nano-crystalline particles are mainly in cube shape or rectangular shape with grain sizes between 40–60 nm, which has smooth surface and little reunion content. Compared with nano-crystalline particles, the amorphous particles are small, dense,

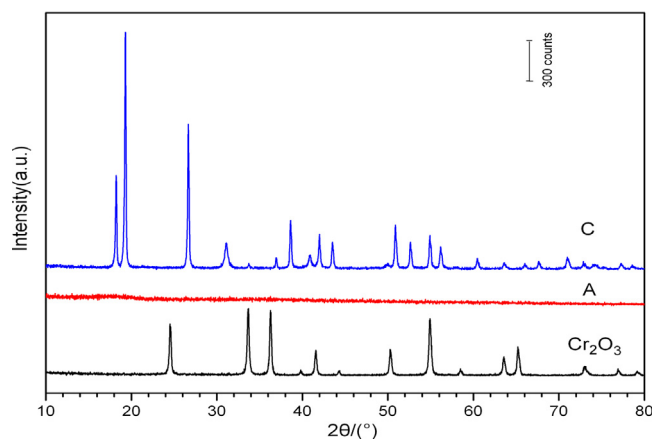


Fig. 1. XRD patterns for crystal- $\text{Cr}(\text{OH})_3$ (C), amorphous- $\text{Cr}(\text{OH})_3$ (A) and Cr_2O_3 .

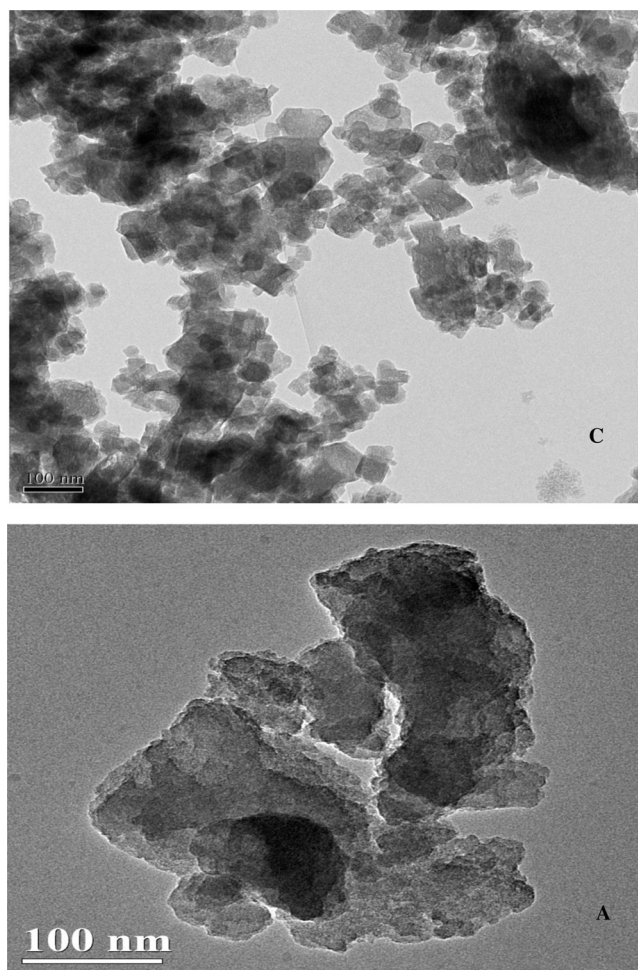


Fig. 2. The HRTEM images of nano-crystalline chromium hydroxide (C) and amorphous chromium hydroxide (A).

irregular, and the particles aggregated greatly. These phenomena are consistent with XRD data.

At 5°C , chromium hydroxide is crystalline because low-temperature conditions are conducive to the reduction of free energy at the grain boundary and to the ordered rearrangement of atoms. In addition, the solution rapidly reaches oversaturation at low temperature. The octahedral structure of trihydrate chromium hydroxide is interlinked by hydrogen bonds, and the octahedral

Download English Version:

<https://daneshyari.com/en/article/1198264>

Download Persian Version:

<https://daneshyari.com/article/1198264>

[Daneshyari.com](https://daneshyari.com)