



Mineralizer effects on the synthesis of amorphous chromium hydroxide and chromium oxide green pigment using hydrothermal reduction method



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ABSTRACT

A chromium oxide green pigment was prepared by thermal decomposition of chromium hydroxide via hydrothermal reduction of a high concentration mixture of Na_2CrO_4 (300 g/L) using NaHCO_3 as a mineralizer. The mineralizer effects on the hydrothermal process, conversion of chromate, properties of amorphous $\text{Cr}(\text{OH})_3$, and color performance of Cr_2O_3 were investigated. Compared with sodium carbonate and urea, sodium bicarbonate significantly reduces the Na_2CrO_4 concentration and, consequently, improves the conversion of Na_2CrO_4 during the hydrothermal process. Additionally, homogeneous particles were obtained by adding NaHCO_3 . The changes in the amount of trapped water, oxygen chemisorption, and negative charge on the surfaces of chromium hydroxide particles caused by adding a mineralizer were analyzed using Fourier-transform infrared spectroscopy and zeta potential analysis. The Cr_2O_3 pigments were characterized using X-ray diffraction, scanning electron microscopy, and an automatic differential colorimeter. A good color performance by the Cr_2O_3 pigment, comparable to that of a commercial pigment, was obtained.

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1. Introduction

Cr_2O_3 is used in a wide range of green pigments, coating materials for thermal protection, catalysts, glass production, and lithium-ion batteries. The traditional process for Cr_2O_3 production involves the reduction of an alkali metal dichromate by ammonium sulfate or the decomposition of chromic anhydride. These processes raise concerns, because of the release of Cr(VI)-containing toxic wastes and pollutant gases into the environment.

Recently, Cr(III) precursors have been prepared for the production of Cr_2O_3 , preventing environmental pollution by wastes and gases. Various Cr(III) precursors, including $\text{Cr}(\text{OH})_3$ [1–4], Cr–ethylene diamine tetraacetic acid (EDTA) complexes [5], Cr–urea complexes [6], chromium hexacarbonyl [7], and chromium trichloride [8] have been investigated to regulate the synthesis of

Cr_2O_3 . In particular, $\text{Cr}(\text{OH})_3$ has been made by hydrothermal reduction of chromate; this process shows great promise for cleaner production, because it is performed in a sealed autoclave to control the reaction atmosphere [9–11]. $\text{Cr}(\text{OH})_3$ was obtained by reduction of 0.0125 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution by acrylamide at 180 °C. Although a high yield (99.4%) was obtained, the reaction time was as long as 12 h [3]. With CrO_3 (<50 g/L) and HCOH as the raw materials, amorphous $\text{Cr}(\text{OH})_3$ was obtained at 170 °C in 1 h [9]. Although the preparation of amorphous $\text{Cr}(\text{OH})_3$ and Cr_2O_3 nanoparticles was investigated in these studies, the mechanism of $\text{Cr}(\text{OH})_3$ formation under hydrothermal condition was unclear. The color performance of Cr_2O_3 obtained by decomposition of $\text{Cr}(\text{OH})_3$ obtained by hydrothermal reduction of chromate was not determined.

Production of $\text{Cr}(\text{OH})_3$ from a high Na_2CrO_4 concentration (300 g/L), based on the leaching liquor from calcium-free roasting of chrome, is less well established. Chromate alkali solutions contain sodium hydroxide, sodium aluminate, and a large amount of sodium chromate. Carbonation was used to remove aluminates, giving sodium chromate solutions containing mineralizers (Na_2CO_3 and NaHCO_3). Mineralizers with high solubilities at preset

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temperatures and pressures are generally used to promote crystallization under hydrothermal conditions [12]. However, there are few reports on mineralizer action in the formation of amorphous $\text{Cr}(\text{OH})_3$ and the chemical equilibrium of various complexes formed between $\text{Cr}(\text{OH})_3$ and mineralizers obtained from reduction of chromate by starch under hydrothermal conditions.

In the current study, a green process for the production and morphology control of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 by hydrothermal reduction using a high concentration of Na_2CrO_4 and various mineralizer concentrations was investigated. An appropriate amount of mineralizer was added to form coarse particles by agglomeration of amorphous $\text{Cr}(\text{OH})_3$, which was washed several times and calcined to obtain pure Cr_2O_3 . The effects of the mineralizer species and concentration on the particle size distributions and morphologies of amorphous $\text{Cr}(\text{OH})_3$ and Cr_2O_3 were examined. Zeta potential and Fourier-transform infrared spectroscopy (FTIR) analysis were used to examine the dispersion performances of amorphous $\text{Cr}(\text{OH})_3$ under various conditions. Finally, the mechanism of the mineralizer action in the formation of amorphous $\text{Cr}(\text{OH})_3$ and the color performance of Cr_2O_3 were investigated.

2. Materials and methods

2.1. Reagents and apparatus

Na_2CrO_4 and mineralizer (Na_2CO_3 , NaHCO_3 and $(\text{NH}_2)_2\text{CO}$) were of analytical reagent grade (Guangdong Xilong Chemical Co., Ltd., China). Starch was obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., China. The autoclave (GSHA-2) used was purchased from Weihai Xintai Chemical Machinery Co., Ltd., China. The muffle furnace used (HY-1400 °C) was purchased from Luoyang Hengyu Experimental Electric Furnace Factory, China.

2.2. Operating procedure

The artificial liquor was prepared by dissolving Na_2CrO_4 (300 g) and different amount of mineralizer in deionized water (1000 mL). Starch was added and the mixture was placed in the autoclave, which was heated at 200 °C for 2.5 h. After the reaction, the product slurry was separated into filtrate and filter cake using a Buchner funnel. The filter cake was washed with deionized water for 30 min at 90 °C. The series of Cr_2O_3 was obtained by calcinations of amorphous $\text{Cr}(\text{OH})_3$ at 950 °C for 2 h.

The residual concentration of Cr(VI) in the filtrate was analyzed by titration. The fraction conversion of Cr(VI) was calculated using the formula:

$$X = (1 - C_r V_r / C_i V_i) \times 100\% \quad (1)$$

where X is the fraction conversion of Cr(VI); C_i and C_r are the initial and residual concentrations of Cr(VI), respectively; V_i and V_r are the initial and residual volumes of the solution, respectively.

2.3. Analysis of amorphous $\text{Cr}(\text{OH})_3$ and Cr_2O_3

After complete washing, the cake was dispersed in the deionized water. The particle size distribution of $\text{Cr}(\text{OH})_3$ was measured by a mastersizer (MS 2000, England). The cake was dried at 105 °C in a drying oven. The surface morphology and particle size distribution of $\text{Cr}(\text{OH})_3$ were investigated using a scanning electron microscope (SEM, JSM 6700F, Japan) and a mastersizer (MS 2000, England), respectively.

FTIR spectra of $\text{Cr}(\text{OH})_3$ were obtained by direct transmittance using the KBr pellet technique. Pellets of ca. 1 mg of $\text{Cr}(\text{OH})_3$ were

prepared by mixing with 100 mg of spectroscopic-grade KBr. The FTIR spectra were recorded using a Nicolet 520P spectrometer equipped with a detector at 4 cm^{-1} resolution and 64 scans per sample. Background spectra were collected using pure KBr. X-ray analysis of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 was performed on a TTRAX3 theta–theta Goniometer (powder X-ray diffractometer, XRD) using Cu K_α radiation in the step mode between 10° and 80° , with a step size of 0.01° and a step time of 0.3 s.

The zeta potentials of amorphous $\text{Cr}(\text{OH})_3$ were measured with the use of a Delsa™ nano zeta potential and submicron particle size analyzer manufactured by Beckman Coulter Inc., USA. To prepare samples for the zeta potential measurements, 0.2 g amorphous $\text{Cr}(\text{OH})_3$ was mixed with 250 mL of distilled water. The mixed suspension was treated by ultrasonic technique at room temperature for several hours. The pH of the diluted suspension was adjusted using HCl or NaOH, and a small quantity of the suspension was transferred to the sample cell of the ZetaPALS for zeta potential measurements.

The color performance data of Cr_2O_3 were reported in the International Commission on Illumination (CIE- $L^*a^*b^*$) colorimetric system. According to the CIE- $L^*a^*b^*$ colorimetric system, the value of CIE- L^* denotes the degree of lightness and darkness of the color in relation to the scale extending from white ($L^* = 100$) to black ($L^* = 0$), the value of CIE- a^* denotes the scale extending from green ($-a^*$) to red ($+a^*$) axis, and the value of CIE- b^* denotes the scale extending from blue ($-b^*$) to yellow ($+b^*$) axis. Values of CIE- $L^*a^*b^*$ color parameters were measured on the Cr_2O_3 samples and standard samples used in the industries with an SC-80C automatic differential colorimeter manufactured by Beijing KangGuang Instrument Co., LTD, China, with an illuminant D65 as required, and a measurement precision of 0.01. For each colorimetric parameter of the determined sample, the final result was the average value calculated by three values measured by the instrument.

3. Results and discussion

3.1. Reaction between sodium chromate and starch

3.1.1. Effect of mineralizer species and concentration on chromate conversion

The hydrothermal reaction between Na_2CrO_4 and starch is shown in Eq. (2). In Fig. 1, the dotted line indicates the conversion of pure sodium chromate by reduction with starch (89.9 wt%). The bar

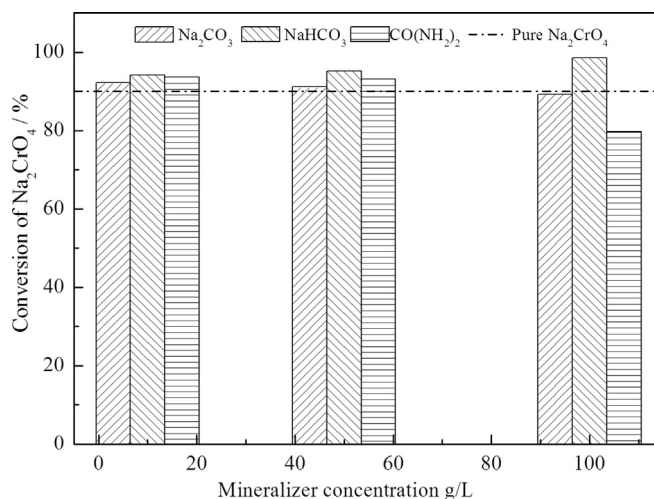


Fig. 1. Effect of mineralizer species and concentration on the chromate conversion. The preset solution was heated at 200 °C for 2.5 h.

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