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Agglomeration behavior of chromia nanoparticles prepared by amorphous complex method using chelating effect of citric acid

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Abstract

Chromia (Cr_2O_3, chromic oxide, Eskolaite) nanoparticles were prepared by amorphous complex method using citric acid as a chelating agent. As a precursor for chromic oxide particle, dried gel with a three-dimensional network consisted of the molar ratio of [citrates]/[chromium ions]=2:1 was prepared. Finally, chromic oxide nanoparticles were formed by calcination of precursor gel at 700 °C for 2 h. Obtained chromic oxide particles were characterized by thermogravimetric and differential thermal analysis, X-ray diffraction, field emission scanning electron microscopy, and Brunauer–Emmett–Teller surface area measurement. It turned out that chromic oxide nanoparticles showed highly agglomerated structure consisted of weakly attached primary particles with each other by van der Waals and capillary adhesive forces. The size distribution of the individual particles was about 20–50 nm. Estimated average particle size from BET surface area was 29.21 nm. The reason for the formation of highly agglomerated structure was discussed.

Keywords: Chromia nanoparticles; Amorphous complex method; Citrate gel method; Citric acid

1. Introduction

The preparation of nanoparticles has attracted a great deal of attention because of its technological applications such as in ceramics, magnetic particles, semiconductors, superconductors, and metallic catalysts. Many inorganic particles of different chemical compositions, shape, and size distribution have been prepared through different mechanical or chemical methods [1].

Because of their nature, chelating agents tend to form complex with metal ions. A chelating agent is a molecule with two or more potential electron-pair donor atoms, that can act as a ligand, which attaches itself to metal ion, such ligands are described as polydentate and the prefix di-, tri-, tetra-, penta-, and hexa are used for two through six bonding positions. Actually, the formation of metal chelate complexes is a Lewis acid-base reaction. Although acid-base reactions generally are enthalpy driven, chelation of solvated metal ions, as an exception, is governed by a relatively high contribution of entropy, due to the replacement of many solvent molecules around a metal ion by one chelating ligand. Due to this behavior, most metal chelate complexes exhibit a relatively high stability [2].

Using this behavior, various preparation methods were investigated by many authors. One such technique is the so-called amorphous complex method, often called the amorphous citrate method or citrate gel method. This technique is based mainly on the formation of metal chelate complexes in solution, followed by elimination of the solvent, resulting in a gel that contains cations of the starting solution. The organic fraction of this gel is removed by calcination process, resulting in a very fine and reactive crystalline oxide powder.

Chromic oxide has widely been used as green pigment [3], heterogeneous catalysts [4], coating materials for thermal protection [5], wear resistance [6], and important refractory material due to its high melting temperature (about 2435 °C) and oxidation resistance, although its sintering ability is very poor and requires special sintering

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conditions to achieve high density [7]. Reduction of particle size is needed for the transparent colorant [3] and improved sintering abilities, i.e. decreased sintering temperature and increased density of sintered powders. This is of particular interest for Cr_2O_3 which is difficult to sinter into high densities due to the high vaporization rate, leading to grain coarsening without densification [7].

Recently, nanosized Cr_2O_3 particles have been prepared by several methods including sol–gel process [7], gas condensation [8], microwave plasma [9] and sonochemical reaction [10], laser induced pyrolysis [11], hydrazine reduction followed by thermal treatments [12], mechanochemical processing [13], and urea assisted homogeneous precipitation [14,15]. However, industrial applications of these methods have some limitations in preparing Cr_2O_3 nanoparticles due to their high cost, low yield, and complicated equipment setup Therefore, a simple and economical method for making nanoparticles is strongly needed.

Citrate gel method is the cost efficient preparation method. This route gives high yield and relatively low cost with simple equipment setup. In this study, as a continuation of our previous research regarding the preparation of chromia nanoparticles by precipitation–gelation reaction [16], chromic oxide nanoparticles were prepared by citrate gel method for the first time. The chromic oxide particles were characterized by thermogravimetric and differential thermal analysis, X-ray diffraction, field emission scanning electron microscopy, and Brunauer–Emmett–Teller surface area measurement. The morphological property and agglomeration behavior of individual particles were discussed.

2. Experimental procedure

2.1. Materials

Chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Aldrich, USA, 99%) as the chromium ion source and citric acid ($C_6H_8O_7$, Aldrich, 99%) as the chelating agent were used as received. The water used in this study was deionized by Milli-Q Plus system (Millipore, France), having 18.2 MΩ electrical resistivity.

2.2. Preparation of chromic oxide nanoparticles

0.2 mol citric acid was added into 100 ml of 1 M chromium (III) nitrate nonahydrate aqueous solution very slowly under mild agitation to keep the molar ratio of [citrates]/[chromium ions]=2:1. After 60 min, this solution was slowly evaporated at 80±2 °C for 4 h and 105±2 °C for 6 h in oil bath and dried at 90 °C for 12 h in convection drying oven successively to obtain dry gel. All these steps were performed in 250 ml glass beaker. After drying, crispy and foamy gel with dark green color was obtained (due to the partial release of nitric–nitrous vapors during the formation of the citrate gel). Finally, this precursor was converted into chromic oxide by calcination at 700 °C for 2 h. Unlike other oxide particles that form the hard aggregates after calcination, chromic oxide particles were formed as soft small granular phase even after calcination. The sample was kept in glass vial before measurement.

2.3. Analysis of chromic oxide nanoparticles

Precursor is converted to chromic oxide by decomposition reaction as the temperature was increased. This decomposition reaction depends on the temperature and the nature of precursor. A thermogravimetric and differential thermal analyzer (SDT 2960 simultaneous DSC-TGA, TA instruments) was used to investigate the decomposition pattern of precursor at a temperature-increasing rate of 10 °C/min in the temperature range of 22–900 °C at a dynamic atmosphere of air (100 ml/min). Field emission scanning electron microscopy (Jeol model JSM-6700 F) was used to investigate the morphology of chromic oxide particles. Glass vial containing chromic oxide particles was lightly shaken, and collapsed small particles were used as the FE-SEM sample. This sample was coated with platinum by sputtering for 120 s at 15 mA. Brunauer–Emmett–Teller surface area measurement (BET, ASAP 2000, Microemritics Instrument) was performed to measure surface area. To verify the preparation of chromic oxide particles, X-ray diffractometry measurement was performed with a MAC Science MXP X-ray diffractometer. The incident wavelength was Cu $K\alpha 1$=1.789 Å, and the detector moved step by step ($\triangle 2\theta$=0.05°) between 10° and 80° 2θ. The scan speed was 2°/min.

3. Results and discussion

3.1. Formation of the precursor

Citrate gel method involves the formation of a metal ion citrate that due to the three ligand nature of the citrate, forms

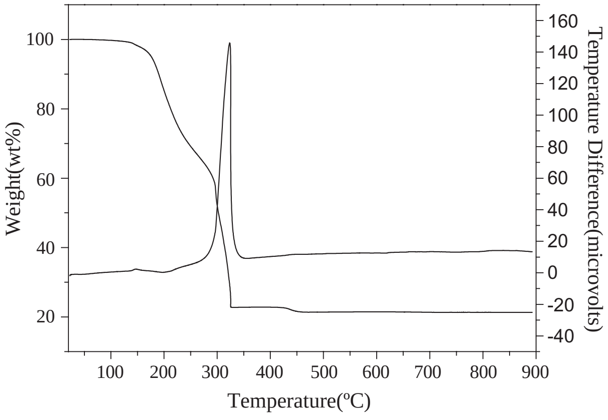

Fig. 1. Simultaneous TGA/DTA of precursor gel prepared by citrate gel method.