Preparation of Cr$_2$O$_3$ nanoparticles via C$_2$H$_5$OH hydrothermal reduction

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Received 21 November 2007; accepted 28 December 2007
Available online 4 January 2008

Abstract

Nanoparticles of chromic oxide (Cr$_2$O$_3$) are widely used in many fields serving as catalysts, wear resistance materials, and advanced colorants. With chromium anhydride (CrO$_3$) and anhydrous alcohol (C$_2$H$_5$OH) as the raw materials, nanoparticles of Cr$_2$O$_3$ were successfully prepared via hydrothermal synthesis. At a reaction temperature as low as 190°C, the redox reaction could be completed within only 1 h. The process needs no stirrer and surfactant and it was easily controllable. The obtained products were loosely agglomerated Cr$_2$O$_3$ nanoparticles with an average particle size ranging from 29 nm to 60 nm. Various approaches including XRD, FE-SEM, TG-DSC, and IR were used to investigate the intermediate and final products. The findings show that a higher calcination temperature tends to result in a smaller specific surface area and a larger average particle size, and a higher ratio of C$_2$H$_5$OH to CrO$_3$ always leads to a higher specific surface area and therefore a smaller average particle size of the products. Moreover, the agglomeration of nanoparticles weakens with the increase of calcination temperature. As the process is simple and low-cost, it has the potential to be produced on a large scale.

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Keywords: Nanoparticles; Hydrothermal synthesis; Cr$_2$O$_3$; Average particle size; Specific surface area

1. Introduction

Nanoparticles of Cr$_2$O$_3$ are widely applied in fields as catalysts [1], advanced colorants [2], hydrogen sorption materials [3], and wear resistance materials [4]. It is necessary to find an economical process which can be used to prepare them on a large scale.

In fact, there have been already a lot of ways to prepare Cr$_2$O$_3$ nanoparticles, including precipitation-gelation process [5], gas condensation [6], sonochemical reaction [7], microwave plasma [8], decomposition of chromium nitrate solution [9], laser-induced deposition [10], but most of them have difficulties in being scaled up due to the more complex processes or more expensive reaction apparatus. A better process should be implored to meet the demands of industrialization.

Hydrothermal synthesis is an usual method to obtain particles on a large scale. Haitao Xu [11] ever obtained Cr$_2$O$_3$ microspheres with the size of 500 nm or so, not in the range of nanometers. In our research, nanoparticles were successfully obtained via hydrothermal synthesis. And the Cr$^{6+}$ concentration of the reactants was about 0.83 mol/L, which was about 31 times higher than that in Haitao Xu’s experiment. The process needs no stirrer and surfactant. And the reaction time was only 1 h, which was much shorter than that in Haitao Xu’s experiment, 18 h. All these advantages endow this process with the potential of industrialization.

2. Experimental procedure

All the reactants are AR grade and used without further purification. Deionized water was prepared from Milli-Q system (Millipore, France).

10 g CrO$_3$ and 5.03 g anhydrous alcohol (C$_2$H$_5$OH) were added to a 200 ml Teflon-lined bomb filled with 120 g deionized water. The mixture was then magnetically stirred to homogeneous solution. The bomb was then sealed with 120 g deionized water. The mixture was then magnetically stirred to homogeneous solution. The sealed bomb was put into an oven and heated at 190°C for 1 h. The hot bomb was then cooled to room temperature. After opening the bomb, brown gel was obtained. It was filtrated and washed for several times until the filtrate turned to be transparent. The filter cake was dried for 10 h and changed to black powders with size in the grade of several μm to mm, which were called Material 1. Material 1 was calcinated at 500°C and 700°C, respectively for 1 h. The former products were black powders but the latter were green ones. All of them were called Material 2. The other experiments were done as above.
3. Analysis

Thermal gravimetric analyzer (STA 449C, NETZSCH) and FT-IR (SPECTRUM GX II, Perkin-Elmer, Powers were diluted in KBr) were used to investigate Material 1. X-ray powder diffractometer (X’ Pert PRO MPD, PANalytical, the Netherlands) using Cu Kα radiation (λ = 1.5408) was used to verify the chromic oxide particles. The specific area surfaces of particles were measured by Brunauer–Emmett–Teller area measurement (BET, ASIMP, Quantachrome), from which mean particle sizes could be obtained through computation. And field-emission scanning electron microscopy (JSM-6700F, Electron Company, Japan) was performed to investigate the morphology of nanoparticles, and high-quality photomicrographs were obtained.

4. Results and discussion

4.1. Verification of Material 1 and Material 2

IR spectra of Material 1 are shown in Fig. 1. It shows that the characteristic bands are 3417, 2969, 2895, 1627, 1448, 1085, 1046, 881, 562 cm⁻¹, respectively. Among them, 3417 cm⁻¹ is due to the OH stretching of nondissociated water molecules and surface hydroxyls of dissociative chemisorption [12]. 2969 and 2895 cm⁻¹ are assigned to intramolecular hydrogen bond derived from OH. 1627 cm⁻¹ is due to the bending modes of nondissociated water molecules. 1448 cm⁻¹ is derived from the adsorption of bidentate carbonates emerged during the reaction process [12]. 1085 and 1046 cm⁻¹ are relatively assigned to the coupling of the stretching vibration of C–C and C–O single bond and Cr–O–Cr vibrations. 881 and 530 cm⁻¹ are due to the torsional oscillations of trapped water molecules [12]. From the above messages, it can be concluded that the formula of Material 1 is Cr(OC₂H₅)x·yH₂O.

Fig. 2 is the TG-DSC curves for the decomposition of the Material 1. The total weight loss is 32%. Through computation, the possible formula of Material 1 is Cr(OC₂H₅)·0.82H₂O. It is amorphous, as Fig. 3(a) shows. The curves also show that the weight loss increases comparatively slowly from room temperature to 540 °C and thereafter keeps constant on the whole until the total weight loss is up to 32%. From the DSC curve, there are two exothermic peaks at 290 and 604 °C. The former is assigned to the oxidation of parts of the organic functional group and parts of water loss. The latter is due to the oxidation of all parts of the organic functional group and total water loss. And then the crystallographic form transforms from amorphism to crystallization.

Fig. 3 shows the XRD patterns of the precursor and Material 2 obtained after calcinating at 500 °C for 1 h. And Fig. 3(b) reveals that Material 2 is crystallized Cr₂O₃, which was obtained by calcinating the precursor, the amorphous Cr(OC₂H₅)·0.82H₂O, as Fig. 3(a) shows.

Then the possible mechanism of the process was concluded as follows:

\[
\begin{align*}
\text{CrO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CrO}_4 \quad (1) \\
\text{H}_2\text{CrO}_4 & \rightarrow 2\text{H}^+ + \text{CrO}_4^{2-} \quad (2) \\
9\text{H}^+ + 8\text{CrO}_4^{2-} + 16\text{C}_2\text{H}_5\text{OH} & \rightarrow 8\text{Cr}(\text{OC}_2\text{H}_5)\cdot0.82\text{H}_2\text{O} + 7\text{CH}_3\text{COO}^- + 2\text{CO}_2 + 15.44\text{H}_2\text{O} \quad (3)
\end{align*}
\]

Fig. 3. XRD patterns of the precursor and Material 2 obtained after calcinating at 500 °C: (a) the precursor and (b) Material 2 (5.03 g C₂H₅OH:10 g CrO₃).
In order to evaluate the average particle size, the formula 
\[ d = \frac{6}{\rho A} \] 
was used [13]. \( d \), \( \rho \) and \( A \) were average particle size, density and the according specific surface area, respectively. The specific surface area could be obtained through the BET measurement. \( \rho \) is 5.21 g/cm\(^3\), as in literature [13].

### 4.2. Morphology and size distribution of the precursor and Cr\(_2\)O\(_3\) nanoparticles

Fig. 4 shows the FE-SEM photographs of Material 1 and Cr\(_2\)O\(_3\) nanoparticles obtained at different reaction conditions and calcination temperatures. Fig. 4(a) is the image of the precursor. It shows that the precursor is made up of variform particles in the size of several \( \mu \)m to mm. But after calcination, the precursor particles decomposed to loosely agglomerated nanoparticles of Cr\(_2\)O\(_3\), as Fig. 4(b) and (c) shows. The comparison of image (b) and (c) also shows that higher calcination temperature can lessen conglomeration of nanoparticles. This result is in agreement with the literature [13].

Table 1 shows influences of reactants ratios and calcination temperatures on the specific surface area and average particle size. In the process, the reaction time of all experiments is 1 h.

From Table 1, two laws can be found. When other factors were kept changeless, higher ration of C\(_2\)H\(_5\)OH to CrO\(_3\) could lead to larger specific surface area. For example, when calcination temperature was 500 °C, the specific surface area of Cr\(_2\)O\(_3\) nanoparticles obtained from reactants whose ratio of C\(_2\)H\(_5\)OH to CrO\(_3\) was 5.03:10 (g/g) was 37.98 m\(^2\)/g, which was larger than that of nanoparticles obtained from reactants whose ratio of C\(_2\)H\(_5\)OH to CrO\(_3\) was 2.53:10 (g/g), 30.64 m\(^2\)/g. When the calcination temperature was 700 °C, experiments obeyed the same law. The second law is that higher calcination temperature can lead to smaller specific surface area when other factors keep the same. For example, when the ratio of C\(_2\)H\(_5\)OH to CrO\(_3\) was 5.03:10 (g/g), the specific surface area of nanoparticles calcinated at 700 °C was 19.09 m\(^2\)/g, which was smaller than that of

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<th>CrO(_3) (g)</th>
<th>C(_2)H(_5)OH (g)</th>
<th>Calcination temperature (°C)</th>
<th>Specific surface area (m(^2)/g)</th>
<th>Average particle size (nm)</th>
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<td>10</td>
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nanoparticles calcinated at 500 °C, 37.98 m²/g. The experiments under other reactants ratios had the same conclusion as above.

5. Conclusion

In the research, nanoparticles of Cr₂O₃ were successfully prepared via hydrothermal synthesis. The obtained nanoparticles were loosely agglomerated with the average size of 29–60 nm. And in the process, there stand two laws. The one is that higher ratio of C₂H₅OH to CrO₃ can lead to larger specific surface area and smaller average particle size. The second is that higher calcination temperature can lead to smaller specific surface area and larger average particle size. And Cr⁶⁺ concentration of reactants was about 0.83 mol/L, much higher than that in literature which provided a way to prepare Cr₂O₃ nanoparticles. The reaction time was only 1 h and need not a stirrer and surfactant during the reaction. The process is so easily controllable and low-cost that it has the potential to be industrialized.

Prime novelty statement

1. C₂H₅OH is a kind of resourceful and nontoxic raw material. No literatures have reported that C₂H₅OH can be used as reducing agent to produce Cr₂O₃ nanoparticles via hydrothermal synthesis. The process is a novel one.

2. The Cr⁶⁺’s concentration of the reactants was about 0.83 mol/L, which was about much higher than that in literature. The process needs no stirrer and surfactant. And the reaction time was only 1 h, which was much shorter than that in Haitao Xu’s experiment, 18 h. All these advantages endow this process with the potential of industrialization.

Acknowledgements

The research was supported by National High-Tech. Research and Development Program of China (Grant No. 2005AA647010) and National Key Technologies Supporting Program of China (Grant No. 2006BAC02A05).

References