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Synthesis and catalytic behaviors of cobalt nanocrystals with special morphologies

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ABSTRACT

Cobalt nanocrystals with highly ordered snowflake-like, cauliflower-like, ball-like morphologies, and some less ordered shapes were prepared through the reduction of $Co(NO_3)_2$ by hydrazine hydrate in the solution of methanol, ethanol, ethylene glycol, and 1,2-propanediol. Based on the characterization results of X-ray powder diffraction and scanning electron microscope, crystal and morphologic structures of cobalt particles were correlated with the reaction conditions of temperature, $Co(NO_3)_2$ concentration, and the alcohols used. By changing temperature and/or $Co(NO_3)_2$ concentration, pure hexagonal close-packed (hcp) cobalt or a mixture of hcp and face-centered cubic (fcc) cobalt was obtained. The catalytic performance of as-prepared cobalt nanocrystals for the thermal decomposition of ammonium perchlorate (AP) was evaluated by differential scanning calorimetry. The decomposition temperature of AP was significantly decreased, and the apparent decomposition heat was over doubled when 2 wt.% cobalt was added into AP. Among the samples tested, snowflake-like cobalt showed the best performance in the aspect of decreasing the decomposition temperature of AP while the ball-like cobalt exhibited the highest apparent decomposition heat.

1. Introduction

Cobalt nanocrystals are of great interest over a long time for researchers from a wide range of fields, including catalysis, high density information storage, solar energy absorption, cell separation, drug delivery, and magnetic sensors, etc [1–5]. So far, the investigated methods for preparing Co nanocrystals are pyrolysis of the cobalt carbonyls [6,7], microemulsion synthesis [8,9], liquid-phase reduction of cobalt salts by hydrazine hydrate [3], sodium borohydride [10] or metallic lithium [11], pulse current electro-deposition [12], etc. Among these methods, the liquid-reduction route is an ambitious method due to its simple and inexpensive nature. Moreover, high-purity cobalt can be obtained by using the reductant of hydrazine hydrate and may have a potential industrial application. By examining the literature results, it can be found that much attention has been paid on the synthesis of nanowire, nanorod, and nanoparticles of cobalt [13–16], and only fewer reports are concentrated on the synthesis of agglomerated forms of cobalt nanocrystals [17]. Qian's group has demonstrated that dendritic nanocrystals of cobalt can be conveniently synthesized in ethanol solution using hydrazine hydrate as a reducing agent at a room temperature [3]. A facile hydrothermal route for the synthesis of highly ordered snowflake-like cobalt microcrystals, in which the precipitated $Co(OH)_2$ is reduced with hydrazine hydrate in a slow-release controlled mode, has recently been reported [18]. The work by Xu et al. [19] shows that the catalytic behavior of the microflowers of nanostructural CuO is quite similar to that of the CuO nanoparticles. Thus, the nanostructural cobalt with different morphologies may have important impacts on its, at least, catalytic applications, for which the processing problems of nanoparticles, e.g., agglomeration and difficult dispersion, can be largely avoided. However, in the literature works, nanostructural cobalts are mainly investigated for their magnetic applications, and the catalytic applications of cobalt nanocrystals with different morphologies, e.g., snowflake-like, cauliflower-like, and ball-like Co, are less studied.

Being cheap and with a large amount of oxygen, ammonium perchlorate (AP, NH_4ClO_4), has extensively been used as an oxidizer in composite propellants for rocket propulsion. Indeed, much work has been done on the catalytic decomposition of AP [20], and the nanosized metals or metal oxides, such as Ni, CuO, and MgO, are found to be good catalysts. Among the investigated additives, metallic cobalt is less studied. However, cobalt nanocrystal with a dendritic morphology shows high catalytic performance in AP decomposition [21], for which is related to its microstructure besides the catalytic nature of cobalt.

In this study, the cobalt nanocrystals with ordered snowflake-like, cauliflower-like, and ball-like morphologies were prepared via the reduction of $Co(NO_3)_2$ by hydrazine hydrate in the solution of different alcohols, and the relationship between the morphology and preparation conditions was correlated. A very high catalytic activity of snowflake-like cobalt nanocrystals towards the decomposition of AP was observed, for which is explained based on the interfaces of cobalt and AP in the composite.

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2. Experimental

All chemicals and reagents used in this work, i.e., hydrated cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), sodium hydroxide, methanol, ethylene glycol, 1,2-propanediol, and anhydrous alcohol, were of analytical purity, and supplied by Xi'an Chemical Co. Ltd. Aqueous hydrazine ($N_2H_4{\cdot}H_2O$, 80 wt.%, AR grade) obtained from the Chengdu Kelong Chemical Reagent Company was used without further purification.

2.1. Preparation of cobalt nanocrystals

The cobalt nanocrystals were prepared by rapidly mixing two solutions for redox reaction under desired conditions. One solution was obtained by dissolving cobalt nitrate into alcohol, and the other solution was prepared by dissolving sodium hydroxide into hydrazine hydrate. In a typical preparation procedure, 1 g of hydrated cobalt nitrate and 1 g of sodium hydroxide were dissolved in 20 mL of anhydrous ethanol and 20 mL hydrazine hydrate, respectively. Then the solutions were mixed together quickly at 50 °C. The color of the mixed solution changed from dark blue to pink, and finally gray black particles were observed. When the solution became transparent, indicating that the reaction was finished, the precipitates were collected by centrifugation, and washed alternately with deionized water and ethanol for three times. After being dried in vacuum at 60 °C for 12 h, cobalt nanocrystals were obtained.

2.2. Preparation of AP and Co composites

Firstly, the as-prepared cobalt nanocrystals were ultrasonically dispersed in 4 mL of anhydrous ethanol for 10 min. Simultaneously, AP was milled in an agate mortar for 15 min. Then, 2 wt.% of cobalt nanocrystals and 98 wt.% of AP were thoroughly mixed and milled in ethanol. After this, the mixture was vacuum-dried until powders formed. Finally, the composite of cobalt and AP was obtained after that the powdery mixture was further milled for 10 min.

2.3. Characterization

The X-ray powder diffraction (XRD) studies were carried out on a Rigaku D/max-3c apparatus with Cu$K\alpha$ radiation (λ=0.154 nm) in a range of 30–90° (2θ), operated at 40 kV and 100 mA. The morphologies of the as-prepared samples were examined by scanning electron microscope (SEM) (QUANT200). The differential scanning calorimetry (DSC) of the selected samples was conducted on a TA-Q1000 under the atmosphere of flowing nitrogen and at a heating rate of 20 °C min^{-1}.

3. Results and discussion

The direct precipitation of metal particles from a solution containing metal precursors is essentially a redox reaction involving the simultaneous processes of nucleation, growth, coarsening, and/or agglomeration. As a result of the sufficiently low solubility of the metal in the solution, supersaturation condition can be easily achieved for nucleation. In an overwhelming majority of precipitation processes, the growth of the formed nuclei is diffusion-limited, which is largely determined by temperatures and concentration gradients [22]. As a result of these factors, the controlled preparation and the detailed mechanistic understanding for the formation of the cobalt nanocrystals with targeted morphologies become a formidable work. Based on the analysis of the general effects of preparation parameters on the precipitation of cobalt particles in the available literature, cobalt nanocrystals with different morphologies were prepared by varying the parameters, i.e., temperature, the concentration of cobalt nitrate, and solvent. More attention was paid on the relationship between morphologies and preparation conditions.

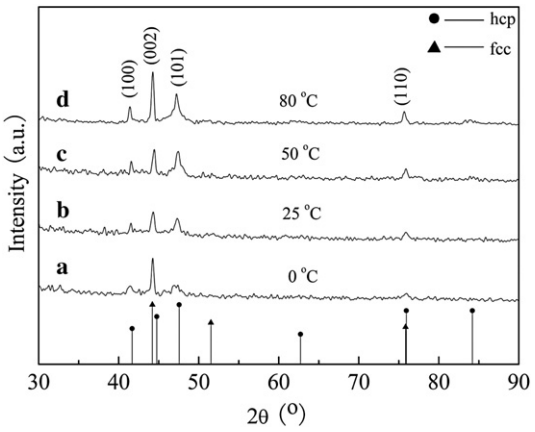

Fig. 1. XRD patterns of cobalt prepared in ethanol solution under the conditions of 0.050 g mL^{-1} $Co(NO_3)_2$ and 20 mL $N_2H_4{\cdot}H_2O$ (80%).

3.1. Reaction temperature

To investigate the effect of temperature on the crystal structure and morphology of cobalt nanocrystals, the redox process was performed at 0 °C, 25 °C, 50 °C, and 80 °C, respectively. The XRD patterns of the obtained cobalt naocrystals are shown in Fig. 1. The metallic cobalt has three crystal structures, i.e., hexagonal close-packed (hcp), face-centered cubic (fcc), and epsilon [7,17]. Irrespective of the temperatures applied, the XRD patterns in Fig. 1 showed the formation of metallic cobalt with hcp structure according to the Joint Committee on Powder Diffraction Standards (JCPDS) Card# 05-0727 (space group: P63/mmc (194), a=2.503 Å, c=4.061 Å). The peaks were well assigned to the (100), (002), (101), and (110) diffractions with plane distances of 2.18, 2.04, 1.93, and 1.26 Å, respectively. Based on these diffractions, the lattice parameters were calculated to be of a=2.521 Å and c=4.080 Å, which are in good consistency with the values in the JCPDS card of hcp cobalt. Moreover, the (002) diffraction gave a higher intensity than it would be, which indicates that the crystallites are abundant in (001) facets and thus their (001) planes tend to be preferentially oriented [23]. It is of interest to find that the intensities of all the diffractions were increased with the increase of the temperature, indicating that the cobalt was better crystallized at higher temperature. Under atmospheric conditions, metallic cobalt can be easily oxidized to form cobalt oxide or cobalt hydroxide. However, some possible cobalt oxides or cobalt hydroxide, e.g. CoO, Co_2O_3, and $Co(OH)_2$, were not observed from the XRD patterns as shown in Fig. 1. To a certain extent, this may be because nitrogen gas produced during the redox reaction could protect the precipitated cobalt in solution against being oxidized. In accordance with these analyses, it can be concluded that the materials obtained by changing only the redox temperature are pure hexagonal-phase metallic cobalt when the concentration of $Co(NO_3)_2$ and the hydrazine hydrate added were kept the same of 0.05 g mL^{-1} and 20 mL, respectively.

The SEM images of the cobalt particles obtained at different temperatures are shown in Fig. 2. It is clear that the prepared cobalt with different morphologies was assembled from the primary particles or subunits as reported in previous work [24]. With the increase of redox temperature from 0 °C to 25 °C, the morphologies of cobalt nanocrystals were transferred from cauliflower-like shape to snowflake-like shape. A further increase of temperature from 25 to 50 or 80 °C, the snowflake-like shape was still reserved. However, at higher temperature, the average size of the snowflake-like cobalt seems to be increased, and more irregular particles were formed and covered on the snowflake-like particles. Thus, there was a significant effect of redox temperature on the morphologies of cobalt nanocrystals. With the available characterization results, we cannot exactly describe how these morphologies were formed. However, it must be