Preparation, characterization and photocatalytic activity of CeO$_2$ nanocrystalline using ammonium bicarbonate as precipitant

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Abstract

CeO$_2$ nanocrystalline was obtained as a final decomposition product of hydrated cerium carbonate formed by using ammonium bicarbonate as precipitant. The decomposition course of hydrated cerium carbonate and the formation process of CeO$_2$ were studied by TG and XRD. Moreover, the effect of the dispersant on the dispersity of the CeO$_2$ powder was studied by SEM. The results show that hydrated cerium carbonate completely decomposes to CeO$_2$ at 300 °C for 2 h, and the crystallinity increases with increasing calcination temperature. The dispersity of the CeO$_2$ powder can be improved by the dispersant. For the first time, CeO$_2$ nanocrystalline was utilized as a photocatalyst for the photocatalytic degradation and decolorization of the dye Acidic Black 10B. The decolorizing rate can reach about 97% under appropriate conditions. Therefore, CeO$_2$ nanocrystalline possesses photocatalytic activity, and shows promising in dye wastewater treatment.

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Keywords: CeO$_2$; Nanocrystalline; Precipitation; Dispersant; Photocatalytic activity

1. Introduction

It is well known that rare-earth oxides have been applied widely in many fields. Among them, cerium dioxide (CeO$_2$) finds numerous applications in catalysts [1], catalyst supports [2], cosmetics materials [3], ceramic materials [4], oxygen gas sensors [5], solid oxide fuel cells [6] and fluorescent materials [7]. Moreover, nano-sized materials have been studied vigorously in recent years because their significant properties are different from the bulk [8]. Therefore, the studies on the preparation and properties of CeO$_2$ nanocrystalline have attracted extensive interests during the last few years.

CeO$_2$ nanocrystalline has been prepared by sol–gel process [9], sonochemical synthesis [10], gas condensation [11] and hydrothermal synthesis [12]. These methods have defects in the complex process and expensive raw materials, so the cost of production is very high and it is difficult to be realized in industrial production.

In this paper, CeO$_2$ nanocrystalline has been obtained as a final decomposition product of hydrated cerium carbonate formed by using ammonium bicarbonate as precipitant. The composition and decomposition course of hydrated cerium carbonate, and the formation process of CeO$_2$ and the dispersity of the particles have been investigated by IR, TG, XRD and SEM. For the first time, CeO$_2$ nanocrystalline was utilized as a photocatalyst for the photocatalytic degradation and decolorization of the dye.

2. Experimental

2.1. Synthesis of CeO$_2$ nanocrystalline

Ce$_2$(CO$_3$)$_3$·nH$_2$O (Industrial Product), nitric acid (65%, A.R.), ammonium bicarbonate (A.R.), and polyethylene glycol 1000 (A.R.) were used as the starting ingredients.

Ce$_2$(CO$_3$)$_3$·nH$_2$O was dissolved in hot nitric acid to form Ce(NO$_3$)$_3$ aqueous solution. The accurate concentration of the Ce(NO$_3$)$_3$ solution was determined by EDTA complexing titrimetry. The experimental temperature was kept at 40 °C by a thermostat. 0.5 mol/L ammonium bicarbonate aqueous was dropped slowly into the Ce(NO$_3$)$_3$ aqueous solution with some dispersant
contained in a glass beaker (200 mL) under violent stirring, and the pH value was kept at about 7. After stirring for 1 h, the mixture was aged for over 2 h, then filtered and washed with distilled-water and a little amount of alcohol. The obtained precipitation was put into an oven and dried at 75 °C for 4 h. Then this precursor was calcined in a muffle furnace at 300–1000 °C for 2 h to obtain CeO₂.

2.2. Characterization

IR spectrum was recorded as KBr pellets on Kithachi260-50 Fourier transform infrared (FT-IR) spectrometer. Thermogravimetric (TG) analysis was carried out with a DT-40 analyzer, at a rate of 10 °C/min under static air conditions in the temperature range 20–800 °C, to analyze the decomposition reaction and phase transformation of cerium carbonate precursor. Phases and crystallization of the samples were identified by X-ray diffraction analysis (XRD) with a Y2000 diffractometer using Cu–Kα radiation. The particle size and dispersity of the samples were investigated with a KYKY 2800B scanning electron microscope (SEM). UV–Vis spectrum of CeO₂ nanocrystalline and absorbency of the dye solution were measured by UV-1200 UV–Vis spectrophotometer.

2.3. Photocatalytic degradation reaction

The degradation reaction was carried out in a 200 mL beaker containing 50 mL of dye Acidic Black 10B solution (its concentration was 10 mg/L) and some amount of CeO₂. Sunshine illumination was used as the irradiator. The suspension was stirred for a certain time, and then centrifuged. The absorbency of the supernatant was measured at the maximum absorption of the dye (λ=620 nm) by UV-1200 UV–Vis spectrophotometer to calculate the decolorizing rate (Dₜ) of dye Acidic Black 10B. 

\[ Dₜ = (1 - A/A₀) \times 100\% \]

Where A shows final absorbency and A₀ shows initial absorbency of the dye solution, here A₀=0.490. The decolorization rate of the dye was used to characterize the photocatalytic activity of CeO₂. After photocatalysis reaction, the suspension was filtered, and the catalyst was dried. Then the dried catalyst was analyzed by IR spectrum to judge whether the dye is absorbed on the surface of the catalyst or degraded completely.

3. Results and discussions

3.1. IR analysis

The FT-IR spectrum of the precursor is shown in Fig. 1. The strong absorption band between 1300 and 1600 cm⁻¹ is due to carbonate ion stretching vibration, the sharp absorption peaks between 600 and 900 cm⁻¹ are due to carbonate ion bending vibration, and the absorption band between 3000 and 3750 cm⁻¹ is due to –OH group of H₂O. These prove that the precursor is hydrated cerium carbonate (Ce₂(CO₃)₃·xH₂O), not the mixed salts of cerium and ammonium carbonates.

3.2. TG analysis

Fig. 2 shows the TG curve of the cerium carbonate precursor. It can be seen that the process of weight loss can be divided into two steps. The first from 85 °C to 200 °C is due to the dehydration of the cerium carbonate precursor and the formation of the anhydrous carbonate. The process of weight loss from 200 °C to 600 °C is due to the formation of CeO₂. The weight loss is due to H₂O evaporation. Table 1 shows the relationship between the crystallite size of CeO₂ and the calcination temperature.

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>300 °C</th>
<th>400 °C</th>
<th>600 °C</th>
<th>800 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size/nm</td>
<td>7.01</td>
<td>8.01</td>
<td>14.18</td>
<td>25.15</td>
<td>34.18</td>
</tr>
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</table>

Table 1 Relationship between the crystallite size of CeO₂ and the calcination temperature
weight loss of the precursor is 9% in this step. The second from 200 °C to 400 °C is due to the decomposition of the anhydrous carbonate and the formation of the CeO$_2$ nanocrystalline. The weight loss is 23.5%. After 400 °C, the weight of the precursor no longer changes, which indicates that the precursor has decomposed completely, and crystalline CeO$_2$ has formed completely. According to TG analysis, the calcination temperature should be above 400 °C in order to obtain pure CeO$_2$.

According to TG analysis, the composition of the precursor is CeO$_2$ 67.5%, CO$_2$ 23.5%, and H$_2$O 9%. So, the cerium carbonate precursor can be shown with Ce$_2$(CO$_3$)$_3$·$x$H$_2$O (x=2.5).

3.3. XRD analysis

Fig. 3 shows the X-ray diffraction patterns of the samples obtained respectively by calcining the cerium carbonate precursors in air at 300 °C, 400 °C, 600 °C, 800 °C and 1000 °C for 2 h. From Fig. 3, it can be seen that the CeO$_2$ nanocrystalline has formed at 300 °C, but the crystalline has not grown completely. When the temperature is above 400 °C, the X-ray diffraction peaks of the samples are in excellent accordance with the powder data in the JCPDS card no. 34-394. According to that, the sample is a cubic phase CeO$_2$ with cell parameters of $a$=5.41134 Å. With an increasing calcination temperature from 300 °C to 1000 °C, no new diffraction peak appears, and the peaks corresponding to CeO$_2$ become stronger and sharper gradually, which indicates that CeO$_2$ has formed at 300 °C and the crystallinity of CeO$_2$ increases with the increase in calcination temperature. These results are consistent with those obtained from the TG analysis.

According to the X-ray diffraction pattern of the sample, the average crystallite size of the sample can be estimated by the Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

Where $D$ is the crystallite size of the sample; $K$ is the Scherrer shape factor, here $K=0.9$; $\lambda$ is the X-ray wavelength, here $\lambda$=1.54178 Å; $\beta$ is the full-width at half-maximum (FWHM) in radiation of the peak, and $\theta$ is the Bragg angle of the X-ray diffraction peak. The average crystallite size of the samples obtained at different calcination temperatures is shown in Table 1. It can be seen that the crystallite size increases with the increasing calcination temperature.

3.4. SEM analysis

The dispersity of the as-synthesized CeO$_2$ powder was observed by SEM and shown in Fig. 4. When polyethylene glycol 1000 is used as dispersant, the particles of CeO$_2$ are nearly spherical in shape and dispersing well, and the crystallite size is about 30 nm in diameter, which is in good agreement with the value calculated by the Scherrer equation. When there is no dispersant, the agglomeration is relatively serious and the grain size is relatively big. According to that, the dispersant can not only improve the dispersity of the CeO$_2$ powder but also decrease its grain size. The reason is that the polyethylene glycol

![Fig. 5. Absorption curve of the as-synthesized CeO$_2$.](image)

![Fig. 6. The UV–Vis spectrums of the initial Acidic Black 10B solution (a) and the supernatant after photocatalytic reaction (b).](image)

Table 2

<table>
<thead>
<tr>
<th>Dosage/mg</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$%</td>
<td>72.04</td>
<td>82.65</td>
<td>88.22</td>
<td>96.94</td>
<td>70.41</td>
<td>63.67</td>
</tr>
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</table>

Irradiation time is 2 h.
1000 (PEG1000) is a big molecule with a straight long chain. Because of its hydrophilic groups including the hydroxyl group and ether group, it can be easily dissolved into water and adsorbed on the surface of the particles of the cerium carbonate precursor, forming a protective film around the particles. This results in a spatial steric effect, reducing the probability of aggregation of the particles. So, the possibility of hard agglomeration of the precursor can be decreased in the drying process. In the following calcination and transition process, PEG1000 can be transformed to CO2 and H2O(g), and removed from the system. These evolved gases can prevent the particles from aggregating effectively. So, CeO2 nanocrystalline with good dispersity can be obtained by adding a certain amount of PEG1000 as a dispersant in the reaction.

3.5. Photocatalytic activity of CeO2 nanocrystalline

UV–Vis spectra of the as-synthesized CeO2 nanocrystalline were measured and shown in Fig. 5. From Fig. 5, it can be seen that the as-synthesized CeO2 nanocrystalline has a strong absorption in the region of 285–365 nm and also a relatively strong absorption in the visible region. So, the as-synthesized CeO2 nanocrystalline was used as the photocatalyst for the photocatalytic degradation and decolorization of the dye Acidic Black 10B. The effect of dosage of CeO2 nanocrystalline on the decolorizing rate is shown in Table 2. It is obvious that the decolorizing rate increases with the dosage of CeO2, and the maximum decolorizing rate is obtained when the dosage is 80 mg. After that, the decolorizing rate decreases with the dosage. The reason is that the excess catalyst leads to the decreasing transmission of the solution, which makes the photocatalytic oxidation–reduction reaction not proceed effectively.

UV–Vis spectrum of the supernatant after photocatalytic reaction was measured and contrasted with that of initial Acidic Black 10B solution. From Fig. 6, it can be seen that the main adsorption peaks of the dye in UV–Vis region have disappeared completely after the photocatalytic degradation. That is, the dye is surely degraded by the photocatalyst for the degradation of the dye Acidic Black 10B, it makes the decolorizing rate reach about 97% under appropriate conditions. This shows that the CeO2 nanocrystalline is promising in dye wastewater treatment.

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References
