Preparation of Ca[B₆O₉(OH)₂]·3H₂O nanomaterials by a phase transformation method and their flame retardant and thermodynamic properties

Jing Liu, Xiu-Ying Ma, Zhi-Hong Liu *

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi’an 710062, China

Abstract

Two kinds of Ca[B₆O₉(OH)₂]·3H₂O morphologies, a nanoflake and an ellipsoidal-like nanostructure, have been prepared by an ultrasound-assisted phase transformation of ulexite in H₂BO₃ aqueous solution. All samples were characterized by XRD, FT-IR, TG–DTA, SEM and chemical analysis. The possible formation mechanism of calcium borate Ca[B₆O₉(OH)₂]·3H₂O was proposed. Furthermore, the flame retardant properties of synthesized Ca[B₆O₉(OH)₂]·3H₂O nanostructures were investigated by a thermal analysis method, demonstrating that the nanoflake sample with smaller size had better behavior than others. Molar enthalpies of solution of prepared Ca[B₆O₉(OH)₂]·3H₂O samples were different because of their different morphologies and sizes. Through an appropriate thermochemical cycle, their standard molar enthalpies of formation were obtained, which decreased in turn from nanoflake to ellipsoidal-like nanostructure and then to flower-like microstructure, showing that their stabilities increased gradually with the increase of Ca[B₆O₉(OH)₂]·3H₂O sizes.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

There are many chemical forms of calcium borates found in nature and synthesized in the laboratory. Some of hydrated calcium borates, such as colemanite (2CaO·3B₂O₃·5H₂O) and priceite (4CaO·5B₂O₃·7H₂O), are useful chemical industrial materials not only in glass, pottery and porcelain enamel industry [1] but also in the flame retardant, which are able to eliminate water at temperatures above 100 °C, so their fire-retardant action is comparable with that of Al(OH)₃ [2].

However, the relatively large size of a calcium borate as the fire protector is hardly dispersed in a polymer matrix, which restrains its uses in industry. In addition, the morphology of material also greatly affects its properties. Therefore, much attention has been paid to the application of nanoparticles. Up to now, there are some reports on the preparation of calcium borates with nanostructures, such as the oval-like 4CaO·5B₂O₃·7H₂O nanostructure assembled by nanoplates [3], 2CaO·B₂O₃·H₂O nanobelts [4], α-4CaO·5B₂O₃·7H₂O nanoflake and spherical-like 4CaO·5B₂O₃·7H₂O nanostructures constructed by nanoflake [5]. Our group also evaluated the flame retardant properties of the synthesized 4CaO·5B₂O₃·7H₂O nanostructures by a thermal analysis method [5].

CaO·3B₂O₃·4H₂O named nobleite is one of calcium borate minerals. Karanovic et al. [6] refined its structure as Ca[B₆O₉(OH)₂]·3H₂O using single-crystal data. Schubert [7] reported the preparation of nobleite with the fine grain size of nominally <75 μm by reaction of aqueous H₃BO₃ slurry with powder lime at 85–105 °C. Liu et al. [8] obtained this product when studying the phase transformation of ulexite in H₂BO₃ solution at boiling point. The CaO·3B₂O₃·4H₂O powder with the particle size lying in 0.2–0.3 μm was also synthesized by wet chemistry method with boric acid and calcium oxide as raw materials at 90–100 °C [9]. However, there are no reports on the preparation of nobleite nanomaterials and their flame retardant and thermodynamic properties.

Thermodynamic property is an inherent attribute of nanomaterials. Previous studies showed that the thermodynamic functions of nanomaterials were related to their morphology and size [10–13].

In this paper, we report the preparation of two kinds of Ca[B₆O₉(OH)₂]·3H₂O morphologies, a nanoflake and an ellipsoidal-like nanostructure, by an ultrasound-assisted phase transformation method, and a flower-like Ca[B₆O₉(OH)₂]·3H₂O microstructure sample has also been synthesized under hydrothermal conditions. Furthermore, their flame retardant properties were evaluated by a thermal analysis method, and their thermodynamic properties were also investigated by solution calorimetry.

2. Experimental

2.1. Preparation of samples

All the chemical reagents used in our experiments were of analytical grade and were used without further purification. Ulexite (NaCa [B₆O₉(OH)₂]·5H₂O) was synthesized referring to literature [14].
Ca[\(\text{B}_3\text{O}_5\text{(OH)}_2\)] \cdot 3\text{H}_2\text{O} nanoflake sample (S1): A mixture of 6.0 g of boric acid, 1.0 g of ulexite, and 50 ml of \(\text{H}_2\text{O}\) was treated ultrasonically at 50 °C for 40 min, which was transferred into a 100 ml Teflon-lined stainless autoclave and heated at 100 °C for 16 h under autogenous pressure, and then cooled to room temperature.

Ellipsoidal-like Ca[\(\text{B}_3\text{O}_5\text{(OH)}_2\)] \cdot 3\text{H}_2\text{O} nanostructure sample (S2): A mixture of 6.0 g of boric acid, 1.0 g ulexite, and 50 ml of \(\text{H}_2\text{O}\) was stirred until homogenous, which was transferred into a 100 ml Teflon-lined stainless autoclave and heated at 100 °C for 20 h under autogenous pressure, and then cooled to room temperature.

Flower-like Ca[\(\text{B}_3\text{O}_5\text{(OH)}_2\)] \cdot 3\text{H}_2\text{O} microstructure sample (S3): 7.5 g of boric acid was dissolved in 25 ml of distilled water to give solution A. Then the mixture of 1.98 g of CaO and 7 ml of ethanol was poured into solution A slowly, forming a homogenous mixture which was continued to heat until boiling for 30 min. The obtained mixture was transferred into a 100 ml Teflon-lined stainless autoclave, which was heated at 100 °C for 48 h under autogenous pressure, and then cooled to room temperature.

All of the above resulting white precipitates were filtered, washed with distilled water and alcohol 3 times respectively, and dried in air at 60 °C for 12 h.

2.2. Characterization of the samples

All samples were identified by X-ray powder diffraction (recorded on a Rigaku D/MAX-IIIC with Cu target at a scanning rate of 8° · min \(^{-1}\) with 2θ ranging from 10° to 70°) and FT-IR spectroscopy (recorded on a Nicolet Nexus 670 FT-IR spectrometer in the range of 400–4000 cm \(^{-1}\) with KBr pellets at room temperature). The sizes and morphologies of the products were investigated by scanning electron microscope (Quanta 200, Philips-FEI). Before SEM imaging, the sample was coated with thin layers of gold. The chemical compositions of the samples were determined by EDTA titration for Ca\(^{2+}\) and by NaOH standard solution in the presence of mannitol for B\(_2\)O\(_3\).

2.3. Flame retardant evaluation

The flame retardant properties of the as-synthesized samples were studied through a thermal analysis method. Wood powder was selected as the blank sample. 20% synthesized Ca[\(\text{B}_3\text{O}_5\text{(OH)}_2\)] \cdot 3\text{H}_2\text{O} samples were added into the triplicate selected wood powders respectively and stirred until homogenous. The thermogravimetric analysis (TGA) for the obtained solid mixture was performed on a SDT Q600 thermal analyzer under \(\text{N}_2\) atmosphere with a heating rate of 10 °C/min.

2.4. Determination of thermodynamic parameters of nanomaterials by calorimetric experiment

The designed thermochemical cycle is shown in Fig. 1. The 1 mol dm \(^{-3}\) HCl(aq) (its concentration of 1.0004 mol dm \(^{-3}\)) was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g · cm \(^{-3}\), its concentration can also be expressed as the form of HCl 54.561H\(_2\)O) solvent can dissolve all components of the reaction (5). Applying Hess’s law, the enthalpy of reaction (5) can be calculated according to the following expression:

\[
\Delta H^\circ(5) = \Delta H^\circ(1) + \Delta H^\circ(2) - \Delta H^\circ(3) - \Delta H^\circ(4) \tag{4}
\]

The standard molar enthalpy of formation can be obtained from the value of \(\Delta H^\circ(5)\) in combination with the standard molar enthalpies of formation of \(\text{H}_4\text{B}_2\text{O}_7\) (s), CaO (s), and H\(_2\)O(l).

All the enthalpies of solution were measured with a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [15,16].
dispersive nanoflakes with the thickness of about 50–100 nm. The sample S2 was the uniform ellipsoidal-like nanostructure, which was assembled by nanosheets with the thickness of about 100 nm. The sample S3 was the flower-like microstructure constructed by sheets with the thickness of 250–300 nm.

3.3. The possible formation mechanisms

Based on the experimental results, the formation mechanisms for both Ca[B6O9(OH)2]·3H2O nanosheets are proposed as follows:

The double salt of NaCa[B5O6(OH)6]·5H2O dissolved gradually in H3BO3 aqueous solution to form a borate solution, and the [B(OH)4]− anion polymerized with [B5O6(OH)6]3− anion forming the polyborate anion of [B6O9(OH)2]2− under hydrothermal conditions, and then the CaO·3B2O3·4H2O product was formed:

\[
\text{H}_3\text{B}O_3 + H_2O \rightleftharpoons [\text{B(OH)}_4]^- + H^+
\]

\[
\text{NaCa}[\text{B}_6\text{O}_9(\text{OH})_2]_6 \cdot 5\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{Ca}^{2+} + [\text{B}_6\text{O}_9(\text{OH})_2]^{2+} + 5\text{H}_2\text{O}
\]

\[
[\text{B}_6\text{O}_9(\text{OH})_2]^{2+} + [\text{B}(\text{OH})_4]^- \rightarrow [\text{B}_6\text{O}_9(\text{OH})_2]^{2+} + 2\text{OH}^- + 3\text{H}_2\text{O}
\]

\[
[\text{B}_6\text{O}_9(\text{OH})_2]^{2+} + \text{Ca}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Ca}[\text{B}_6\text{O}_9(\text{OH})_2] \cdot 3\text{H}_2\text{O}.
\]

When the reaction mixture was ultrasonically treated, Ca[B6O9(OH)2]·3H2O nanoflakes were formed through conventional nucleation and crystal growth process. It is the ultrasonic effect that leads to the formation of dispersive Ca[B6O9(OH)2]·3H2O nanoflakes.

When the reaction mixture was not ultrasonically treated, CaO·3B2O3·4H2O nanosheets were firstly formed through conventional nucleation and crystal growth process. Subsequently, nanosheets were aggregated forming the ellipsoidal-like nanostructure. From the view of thermodynamics, the larger the surface area, the higher the surface energy, and the less stable the nanostructure. Thus, with the further prolonging of reaction times, the nanosheets tended to overlap and lower the surface energy by reducing exposed areas, which resulted in the formation of the ellipsoidal-like nanostructure at 20 h.

3.4. The flame retardant tests

Fig. 6 shows TG curves of wood powder, wood powder with 20% prepared Ca[B6O9(OH)2]·3H2O samples S1, S2 and S3, respectively. The corresponding mass losses at different temperatures are listed in Table 2.

As shown in Fig. 6, all the mixture samples have a two-step mass loss between (30 and 700) °C. The first mass loss at (30 to 200) °C corresponds to the loss of adsorbed water in wood powder. The second mass loss at (200 to 700) °C corresponds to the decomposition of wood. It can be seen from Table 2 that the final mass losses at 700 °C are gradually increased, namely, 69.59% for a, 70.59% for b, 73.27% for c, and 80.37% for d. Furthermore, the mass losses at any same temperatures in the range of (200 to 700) °C are also gradually increased from samples a to d, indicating that the decomposing rates are gradually increased from samples a to d. These results show that the borate Ca[B6O9(OH)2]·3H2O has excellent flame retardant property. Moreover, the flame retardant properties of prepared Ca[B6O9(OH)2]·3H2O samples are increased gradually from flower-like Ca[B6O9(OH)2]·3H2O microstructure to ellipsoidal-like nanostructure then to nanoflake, which may be ascribed to their sizes being decreased accordingly. The smaller size of nanostructure and the more uniform morphology, the better flame retardant property of the sample. The smaller size of sample can benefit its good dispersion in the powder and increase its contact area with wood powder, which ultimately improves the flame retardant property.

3.5. The thermodynamic parameters of as-prepared samples

Table 3 gives the thermochemical cycle used for the derivation of the standard molar enthalpies of formation of Ca[B6O9(OH)2]·3H2O for samples S1, S2, and S3. It can be seen that the molar enthalpies of solution of prepared Ca[B6O9(OH)2]·3H2O samples for S1, S2 and S3 in HCl(aq) at 298.15 K are different because of their different morphologies and sizes. The molar enthalpies of solution of prepared Ca[B6O9(OH)2]·3H2O samples increased gradually with the increase of sizes. The molar enthalpies of solution of H3BO3(s) of (21.84 ± 0.05) kJ mol⁻¹ in 2.00 cm³ of 1 mol dm⁻³ HCl(aq), and of Ca(OH)₂ of (–188.59 ± 0.42) kJ mol⁻¹ in 2.00 cm³ of (HCl + H3BO3) aqueous solution were taken from literature[15]. The enthalpy of dilution of HCl (aq) was calculated from NBS tables [18].

![Fig. 3. The FT-IR spectra of samples: (a)S1; (b) S2; (c)S3.](image)

![Fig. 4. TG curves of samples: (a)S1; (b) S2; (c)S3.](image)

<table>
<thead>
<tr>
<th>Weight/%</th>
<th>CaO</th>
<th>B2O3</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>16.64</td>
<td>61.98</td>
<td>21.38</td>
</tr>
<tr>
<td>Experimental (S1)</td>
<td>16.47</td>
<td>61.62</td>
<td>21.36</td>
</tr>
<tr>
<td>(S2)</td>
<td>16.52</td>
<td>61.86</td>
<td>21.10</td>
</tr>
<tr>
<td>(S3)</td>
<td>16.43</td>
<td>61.64</td>
<td>21.18</td>
</tr>
</tbody>
</table>
The enthalpy changes for the formation of Ca[\(\text{B}_6\text{O}_9\text{(OH)}_2\)]·3\(\text{H}_2\text{O}\) from the reagents in the solid phase (reaction 5) were calculated to be \(- (96.79 \pm 0.54) \text{kJ mol}^{-1}\) for S1, \(- (99.07 \pm 0.60) \text{kJ mol}^{-1}\) for S2, and \(- (103.16 \pm 0.57) \text{kJ mol}^{-1}\) for S3 on the basis of the thermochemical cycle. The standard molar enthalpies of formation of \(\text{H}_3\text{BO}_3\)(s), \(\text{H}_2\text{O}(l)\) and \(\text{CaO}(s)\) were taken from the CODATA Key Values [19], namely \(- (1094.8 \pm 0.8) \text{kJ mol}^{-1}\), \(- (285.830 \pm 0.040) \text{kJ mol}^{-1}\) and \(- (634.92 \pm 0.90) \text{kJ mol}^{-1}\), respectively. From these data, the

Fig. 5. The SEM images of samples: (a, b) S1; (c, d) S2; (e, f) S3.

Fig. 6. TG curves of samples: (a, b and c) wood powder with 20% prepared Ca[\(\text{B}_6\text{O}_9\text{(OH)}_2\)]·3\(\text{H}_2\text{O}\) samples S1, S2 and S3, respectively; (d) wood powder.

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>(T/^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>a</td>
<td>8.98</td>
</tr>
<tr>
<td>b</td>
<td>9.16</td>
</tr>
<tr>
<td>c</td>
<td>9.28</td>
</tr>
<tr>
<td>d</td>
<td>9.61</td>
</tr>
</tbody>
</table>

* (a, b and c) wood powder with 20% prepared Ca[\(\text{B}_6\text{O}_9\text{(OH)}_2\)]·3\(\text{H}_2\text{O}\) samples S1, S2 and S3, respectively. (d) wood powder.
standard molar enthalpies of formation of Ca[B₆O₉(OH)₂] · 3H₂O were calculated to be –(5873.6 ± 4.9) kJ mol⁻¹ for S₁, –(5873.6 ± 4.9) kJ mol⁻¹ for S₂, and –(5877.7 ± 4.9) kJ mol⁻¹ for S₃, respectively. It is found that the standard molar enthalpies of formation increase in turn from sample S₃ to S₁, which indicates the decrease of stability with the decrease of Ca[B₆O₉(OH)₂] · 3H₂O sizes.

### 4. Conclusions

In summary, two kinds of Ca[B₆O₉(OH)₂] · 3H₂O nanostructures have been prepared by a phase transformation of ulexite in H₃BO₃ aqueous solution, which had the better flame retardant properties than the Ca[B₆O₉(OH)₂] · 3H₂O microstructure confirmed by TG method. The standard molar enthalpies of formation of prepared Ca[B₆O₉(OH)₂] · 3H₂O samples increase with the decrease of sample sizes, which shows that their stabilities decrease gradually.

### Acknowledgments

This project is supported by the National Natural Science Foundation of China (no. 21173143).

### Table 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>ΔfH° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>6H₄BO₄(s) + 144.738(HCl 54.561H₂O) = 6H₃BO₃(aq) + 144.738(HCl 54.561H₂O)</td>
<td>131.04 ± 0.30</td>
</tr>
<tr>
<td>2.</td>
<td>CaO(s) + 6H₃BO₃(aq) + 144.738(HCl 54.561H₂O) = CaCl₂(aq) + 6H₃BO₃(aq) + 144.738(HCl 55.332H₂O)</td>
<td>–188.59 ± 0.42</td>
</tr>
<tr>
<td>3.</td>
<td>144.738(HCl 54.561H₂O) = 144.738(HCl 54.561H₂O) + 5H₂O(l)</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>4.</td>
<td>Ca[B₆O₉(OH)₂] · 3H₂O(s) + 144.738(HCl 54.561H₂O) = CaCl₂(aq) + 6H₃BO₃(aq) + 144.738(HCl 55.332H₂O)</td>
<td>39.14 ± 0.17</td>
</tr>
<tr>
<td>5.</td>
<td>CaO(s) + 6H₃BO₃(s) = Ca[B₆O₉(OH)₂] · 3H₂O(s) + 5H₂O(l)</td>
<td>42.6 ± 0.12</td>
</tr>
</tbody>
</table>

*ΔfH° (Ca[B₆O₉(OH)₂] · 3H₂O, s) = ΔfH° (5) + ΔfH° (CaO, s) + 6ΔfH° (H₃BO₃, s) – 5ΔfH° (H₂O, l).*  
*The uncertainty in ΔfH° is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.*  
*The uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.*

### References