BASIC PRECIPITATION OF SIMONKOLLEITE NANOPlatelets

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Abstract

Simonkolleite of formula Zn₅(OH)₈Cl₂·H₂O belongs to the layered hydroxide salts (LHS) family. This paper presents a simple precipitation method to produce nanoparticles of simonkolleite. The particles were synthesized by basic precipitation of zinc chloride by sodium hydroxide in aqueous media. The particles were analyzed by atomic force microscopy (AFM), thermogravimetry (TGA), powder X-ray diffraction (XRD), and chemical quantitative analysis. AFM analysis showed the plate-like shape of the particles, with a thickness of 5-10nm, and a diameter of 70-80nm. Chemical analysis, XRD, and TGA confirmed the simonkolleite nature of the product. The presented synthesis method is simple and easily reproducible, and allows the use of additives and modifiers to produce a wide range of modified simonkolleite nanoparticles.

Keywords: simonkolleite, nanoplatelets, layered zinc hydroxide, basic zinc oxide, basic precipitation

1. INTRODUCTION

Simonkolleite of formula Zn₅(OH)₈Cl₂·H₂O [1], belongs to the family of layered hydroxide salts (LHS) of general formula : M(OH)₂-x(Aᵐ⁺)ₓ/m·nH₂O. The similar family of layered double hydroxides (LDH) of formula M²⁺₁₋ₓM³⁺ₓ(OH)₂(Aᵐ⁻)ₓ/m·H₂O, as well as LDH, have been studied due to their layered structure, and the possibility to intercalate selectively or not different organic molecules in their interlayer space, by anionic exchange [2]. LDH and LHS can be used for many applications: catalysts [3], water pollutant removal, separation of isomers [4], drug carriers [5], nanofillers, UV protection [6], mixed metal oxides precursors [7], flame retardants [8]... Among LHS, simonkolleite and other layered zinc hydroxide salts have been studied because of their interesting catalyst support [9], drug carrier [10], UV and visible light absorption [11], and corrosion inhibition [12] properties.

2. SYNTHESIS

ZnCl₂ was first dried at 105°C, and NaOH was used without further preparation. 50ml of a solution of NaOH into distilled water at 0,5 mol/L was prepared, and heated to 45°C at least 30min. Then 30 ml of a solution of ZnCl₂ into distilled water at 0,6 mol/L was injected at once in the reactor containing NaOH solution. The reaction was carried out at 45°C for 42 hours under mechanical stirring and the reactor was sealed to avoid water evaporation.

The formed precipitate was then filtered and washed with a mix of ethanol and distilled water at 1:1 vol, using a microsized paper filter. Cl⁻ was considered the major impurity, and its presence in the filtrate was tested by AgNO₃. Once clean, the precipitate was dried at ambient air during 3 days.

3. COMPOSITION AND PURITY

Four samples were prepared and tested, to ensure the reproducibility of the experiment. Quantitative chemical analysis revealed the global atomic composition of the samples in weight percentage, which are compared to the theoretical simonkolleite composition (Table1). The samples contain traces of Na, a slight excess of Cl and OH, and a lack of Zn. This might be due to traces of ZnCl₂ and Zn(OH)₂ in the samples.
**Table 1** Elementary composition of synthesized samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Zn</th>
<th>%OH</th>
<th>%Cl</th>
<th>%H2O</th>
<th>%Na</th>
<th>%Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58.8</td>
<td>25.7</td>
<td>13.8</td>
<td>1.5</td>
<td>0.12</td>
<td>99.9</td>
</tr>
<tr>
<td>2</td>
<td>58.3</td>
<td>25.4</td>
<td>13.5</td>
<td>0.9</td>
<td>0.11</td>
<td>98.2</td>
</tr>
<tr>
<td>3</td>
<td>57.8</td>
<td>24.6</td>
<td>13.4</td>
<td>2.9</td>
<td>0.11</td>
<td>98.7</td>
</tr>
<tr>
<td>4</td>
<td>56.5</td>
<td>24.6</td>
<td>14.0</td>
<td>3.3</td>
<td>0.12</td>
<td>98.5</td>
</tr>
<tr>
<td>Zn5(OH)8Cl2.H2O</td>
<td>59.3</td>
<td>24.6</td>
<td>12.9</td>
<td>3.2</td>
<td>0.00</td>
<td>100.0</td>
</tr>
</tbody>
</table>

XRD analysis showed a major crystalline part of simonkolleite, which supports the results obtained by chemical analysis. No traces of other phases were detected by XRD (Fig. 1).

Thermogravimetric analysis also supported the chemical analysis, by reproducing the thermal behavior of standard simonkolleite under the same experimental parameters. (Fig. 2) The thermogravimetric analysis was performed at a heating rate of 10°C/min, from 25 to 1000°C under a N2 flow. As reported in literature [13], three decompositions theoretically occur:

- Zn5(OH)8Cl2.H2O $\rightarrow$ 3ZnO + 2β-Zn(OH)Cl + 4H2O at 170°C, 13% weight loss
- 2β-Zn(OH)Cl $\rightarrow$ ZnO + ZnCl2.0,25H2O + 0,75H2O at 220°C, 2,5% weight loss
- ZnCl2.0,25H2O $\rightarrow$ 0,25 ZnO + 0.5HCl + 0.75 ZnCl2 above 230°C, 21,8% weight loss

However, only two weight loss are detected with our samples, and the limit between the two weight loss is not clearly determined, since no horizontal plateau is observed.

4. **SHAPE AND SIZE**

The shape a size of synthesized particles were measured by AFM. All particles presented a platelet shape with a thickness of 2-5nm, and a diameter of 70-80nm(Fig.3). Some agglomerates were observed, showing an improvable dispersion of the particles in the media(Fig.4).
CONCLUSION

Nanoplatelets of simonkolleite were synthesized using a simple precipitation method. Analyses tested their composition and size, and proved the good quality of the particles, as well as the reproducibility of the synthesis. The synthesized nanoplatelets can be modified for different applications by grafting catalysts or stabilizers on its surface, but also intercalating different molecules between its layers. The synthesized sample can also be used as a nanostructured precursor for ZnO synthesis via thermal or hydrothermal phase transformation.[13] The presented method is easy to reproduce, do not require any additives or aggressive conditions. It therefore allows the use of many additives and modifiers, and can be used as a starting point for the synthesis of a wide range of modified simonkolleite or zinc oxide nanoparticles.

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REFERENCES


