Preparation and characterization of organic - inorganic layered nano hybrids by the self-assembly reaction of amino acid and metal hydroxide

Kazuya Shishito, Hajime Fukuda and Hideyuki Tagaya*
Graduate School of Science and Engineering, Yamagata University, Jonan, Yonezawa, Yamagata, 992-8510 Japan
* Fax: 81-238-26-3413, e-mail: tagaya@yz.yamagata-u.ac.jp

Layered organic – inorganic nano hybrids were prepared by the self-assembly reaction of magnesium hydroxide and calcium hydroxide with L-phenylalanine. Layered structures were confirmed by TEM images directly. Interlayer spacing of the layered hybrid was 1.61 nm in the case of magnesium hydroxide and 1.65 nm in the case of calcium hydroxide. It indicates the presence of bi layer structure of L-phenylalanine between the layers. Self-assembly reaction was also confirmed in the reaction of L-phenylalanine with the mixture of magnesium and calcium hydroxides. Interlayer spacing increased with an increase in the amount of calcium hydroxide from 1.61 nm to 1.65 nm.

Key words: Self-assembly reaction, metal hydroxide, amino acid, organic-inorganic layered hybrid, dolomite

1. INTRODUCTION

Much research has been carried out on the preparation of organic and inorganic hybrids organized at the nano level of organic and inorganic molecules. They offer useful new properties compared to conventional materials as functional compounds with high possibilities [1-5].

The intercalation reactions involving layered host lattices have been extensively investigated [6-9]. Intercalation reaction as shown in Figure 1 provides a widely variable method for low temperature preparation of new meta-stable materials which are not accessible by other techniques, which often require temperatures in excess of 873K. Remarkably, a wide range of host lattices has been found to undergo these low temperature reactions and systematic variations of physical properties can be achieved by intercalation [10-12]. However, intercalation of bulky organic compounds into the lattices is not easy and morphology of the obtained hybrid limited to that of host layered compounds.

2. EXPERIMENTAL

Amino acid and metal hydroxide such as magnesium hydroxide and calcium hydroxide was stirred in flasco and refluxed in the solution of acetonitrile 2 ml / water 18 ml mixture at 333 K for 5 h. The molar ratio of amino acid to metal hydroxide is 1.0. The product was collected by filtration after the precipitation. The solid product was washed with distilled water and dried under reduced pressure. The resulting powders were characterized by TG, powder XRD, and TEM.

We have already reported an alternative preparation method of a layered organic-inorganic nano level hybrid with the self-assembly reaction of metal hydroxide with organic carboxylic acid under mild conditions [13-15]. Bulky organic compounds could react with zinc hydroxide giving layered hybrids easily, and morphology such as plate type and needle type depended on the reaction conditions.

In this study self-assembly reactions of magnesium hydroxide and calcium hydroxide with L-phenylalanine were investigated to obtain new hybrids.

Figure 1 Preparation of organic – inorganic nano hybrids by intercalation and self-assembly reaction.

Figure 2 TG curves of (a) calcium hydroxide, (b) L-phenylalanine, (c) the reaction product of calcium hydroxide with L-phenylalanine, (d) magnesium hydroxide, and (e) the reaction product of magnesium hydroxide with L-phenylalanine.
3. RESULTS AND DISCUSSION

3.1 Reaction of calcium hydroxide with L-phenylalanine

In the reaction of L-phenylalanine with calcium hydroxide, the production of new compound was suggested by TG curve of the product as shown in Figure 2 (c). The weight loss curve was different from those of L-phenylalanine and calcium hydroxide clearly.

Weight loss at below 423 K and weight loss at about 650K were suggested to correspond to the weight loss by the desorption of water and decomposition of included L-phenylalanine, respectively. Desorption of water shows the presence of pore structure to possess water among the layered matrix. In the case of calcium hydroxide, weight loss was observed also at about 873K. It was suggested to correspond to the weight loss by the desorption of carbon dioxide.

The molar ratio of L-phenylalanine to calcium hydroxide before the reaction was 1.0. After the reaction the value decreased slightly to 0.7 which was estimated by TG curve as shown in Figure 2 (c).

![Figure 3 XRD patterns of (a) calcium hydroxide, (b) L-phenylalanine, (c) the reaction product of calcium hydroxide with L-phenylalanine, (d) magnesium hydroxide, and (e) the reaction product of magnesium hydroxide with L-phenylalanine.](image)

XRD pattern of the product shows the clear peak at 1.65 nm as shown in Figure 3 (c). In the case of hybrid compounds composed of metal hydroxide such as zinc hydroxide, TEM images could be measured if the compounds are thermally stable [16]. We have already confirmed that hybrids composed of calcium hydroxide are thermally stable compared to hybrids composed of zinc hydroxide and magnesium hydroxide [16].

Certainly in the case of the reaction products of calcium hydroxide with L-phenylalanine, the presence of the layered structure was confirmed directly by the TEM image as shown in Figure 4. The layer distance in TEM image correlated well with the interlayer spacing observed in XRD patterns. It was concluded that layered nanohybrids were produced even in the reaction of calcium hydroxide with L-phenylalanine.

3.2 Reaction of magnesium hydroxide with L-phenylalanine

Similar to calcium hydroxide, the production of new compound was confirmed in the reaction of L-phenylalanine with magnesium hydroxide as suggested by TG curve in Figure 2 (e). It shows that weight loss curve was different from those of raw materials, L-phenylalanine and calcium hydroxide. Also XRD pattern shows the clear peak at 1.61 nm as shown in Figure 3 (e). From these results, the production of layered nanohybrids was also confirmed also in the reaction of magnesium hydroxide with L-phenylalanine. The interlayer spacing of magnesium hybrid was 1.61 nm and lower than 1.65nm of calcium hybrid because thickness of hydroxide layer of magnesium hydroxide was thinner than calcium hydroxide.

3.3 Reaction of the mixture of calcium hydroxide and magnesium hydroxide with L-phenylalanine

Dolomite is well known naturally occurring minerals composed of calcium and magnesium carbonate. After the calcination and water treatment, slaked dolomite is obtained and it is composed of the mixture of calcium hydroxide and magnesium hydroxide.

![Figure 5 TG curves of (a) calcium hydroxide, (b) magnesium hydroxide, (c) L-phenylalanine, and the reaction products of the mixture of calcium hydroxide and magnesium hydroxide with L-phenylalanine. The calcium hydroxide / magnesium hydroxide ratios are (d) 9 : 1, (e) 2 : 1 and (f) 1 : 9.](image)
In this study, L-phenylalanine was reacted with the mixture of calcium hydroxide and magnesium hydroxide to obtain information on the reactivity and characteristics of artificial dolomite. The mixtures of calcium and magnesium hydroxides were reacted with L-phenylalanine in the calcium hydroxide / magnesium hydroxide ratios of 9:1, 2:1 and 1:9.

Thermal characteristics of obtained precipitates were measured. TG curves show the production of new compounds as shown in Figures 5 (d), (e) and (f). In the weight loss pattern of (d) and (e), three step decrease of weight was observed. As a result the weight loss patterns of Figures 5 (d) and (e) was similar to that of Figure 2 (c).

EDS spectra of the reaction products show calcium / magnesium ratios of the products as shown in Figure 6. The ratios were 92.8/7.2, 52.3/47.7 and 9.4/90.6, respectively. The values indicated that the calcium / magnesium ratios of the products were almost similar to the injected calcium / magnesium ratios of raw materials.

Figure 7 shows the XRD patterns of the reaction product of the mixture of calcium hydroxide and magnesium hydroxide with L-phenylalanine. Interlayer spacing increased with an increase in the amount of calcium hydroxide.

TEM image of the reaction product of the mixture of calcium hydroxide and magnesium hydroxide with L-phenylalanine was shown in Figure 8. Clear layer structure was observed. Layer distances of all portions were the same indicating that calcium and magnesium reacted without deviation.

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Figure 7 shows the XRD patterns of the reaction product of the mixture of calcium hydroxide and magnesium hydroxide with L-phenylalanine. Interlayer spacing increased with an increase in the amount of calcium hydroxide.

The structure was similar with that of intercalation compound into layered double hydroxide (LDH) [17, 18]. In the case of LDH, amino acid is intercalated between the layers by ion – ion interactions. However, in the case of

Figure 8 TEM image of the reaction product of the mixture of calcium hydroxide and magnesium hydroxide (2:1) with L-phenylalanine.

3.4 Structural images of nano hybrids

TEM images, Interlayer spacing and the size of L-phenylalanine suggest the bi layer structure of L-phenylalanine between the layers as shown in Figure 9. The structure was similar with that of intercalation compound into layered double hydroxide (LDH) [17, 18]. In the case of LDH, amino acid is intercalated between the layers by ion – ion interactions. However, in the case of

Figure 9 Structural images of the reaction products of (a) calcium hydroxide and (b) magnesium hydroxide with L-phenylalanine.
self-assembly reaction, amino acid was reacted with hydroxyl groups resulting in surface modified layered compounds.

4. CONCLUSIONS

In this study, layered organic - inorganic layered nano hybrids were prepared by the self-assembly reaction of magnesium hydroxide and calcium hydroxide with L-phenylalanine. Interlayer spacing of the surface modified hybrids were 1.61 nm in the case of magnesium hydroxide and 1.65 nm in the case of calcium hydroxide, respectively indicating the bi layer structure of L-phenylalanine between the layers.

Self-assembly reaction was also confirmed in the reaction of L-phenylalanine with the mixture of magnesium and calcium hydroxides. The mixed compounds of magnesium hydroxide and calcium hydroxide are model compounds of slaked dolomite. Interlayer spacing of the hybrids increased with an increase in the amount of calcium hydroxide.

REFERENCES

[16] H. Fukuda and H. Tagaya, 6th International Conference on Green and Sustainable chemistry, P36, Nottingham, United Kingdom (2013)

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