

Conversion of Zinc-containing Layered Double Hydroxide to Chiral Zincophosphate Zeolite

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Conversion of zinc-containing layered double hydroxide (LDH) to chiral zincophosphate (CZP) has been investigated under hydrothermal conditions in aqueous suspension system with sodium hydrogen phosphate. The chiral phase was successfully obtained under conditions at 110 °C and pH 11. About 40 hours were required for complete conversion to CZP. Chemical analysis for the final products revealed that the composition of the solid can be represented as a formula $\text{NaZnPO}_4 \cdot n\text{H}_2\text{O}$ (n : 1.3~1.6) and that the trivalent cations of starting materials were dissolved into the solution phase. XRD pattern of the product was indexed with one of hexagonal unit cells of space groups $P6_1$, $P6_5$, $P6_122$ or $P6_522$. Rietveld refinement for powder XRD supported the framework model of Zn-O-P linkage essentially identical with CZP in the literature. Unit cell parameters were calculated as $a = 1.04730(4)$ nm and $c = 1.50631(4)$ nm. The size and habit of the crystal obtained were found to vary depending on the initial state of the suspension, as well as the starting LDHs used. By using Zn/Al-LDH as the starting material and ultrasonic pre-treatment for the initial suspension, we obtained well-grown crystals with typical dimension of $0.2 \text{ mm} \times 0.2 \text{ mm} \times 1.0 \text{ mm}$ and habit of capped hexagonal-prismatic rod.

Key words: Layered double hydroxide, Chiral zincophosphate, Rietveld refinement, Crystal growth

1. INTRODUCTION

Chiral zeolite is of great interest with respect to stereoselective separations and syntheses,⁽¹⁾ additionally to optical devices such as non-linear optical devices. Control of the crystal size and habit is very important for these applications. However, chiral zincophosphates reported in the literature were small and less homogeneous crystals; the reported sizes were $0.05 \text{ mm} \times 0.05 \text{ mm} \times 0.6 \text{ mm}$ ⁽²⁾ and $0.12 \text{ mm} \times 0.06 \text{ mm} \times 0.04 \text{ mm}$.⁽³⁾ Thus, it is still important to prepare the large and homogeneous crystals for applications. Recently, we reported the conversion from zinc-containing LDH to zincophosphate sodalite.⁽⁴⁾ LDH is double hydroxide of di- and trivalent cations containing anions and water molecules in the interlayer region.⁽⁵⁾ This method to use LDH can produce microporous materials under different reaction conditions from conventional method. Thus, this method is considered to have a possibility to produce crystals in different size and morphology from conventional method. By developing this method, we expected to obtain large crystals of CZP.

In this paper, we demonstrate conversion of zinc-containing LDH to CZP and discuss the relation between morphology and reaction conditions.

2. EXPERIMENTAL

2.1 Materials

Zinc-containing LDH, $\text{Zn}_2\text{M}(\text{OH})_6(\text{CO}_3)_{0.5} \cdot 1.5\text{H}_2\text{O}$ (M; Al and Ga) was prepared with the conventional coprecipitation method.⁽⁶⁾ The structure of the Zn/Al-

CO_3 -LDH was assigned in space group of $R\bar{3}m$ with $a = 0.3068$ and $c = 2.267$ nm. The LDH powder of 1.0 g and Na_2HPO_4 of 1.3 g were added in 10 cm^3 deionized water, respectively. After the LDH suspension was added to the phosphate solution in a 25 cm^3 Teflon bomb, the bomb was sealed with stainless steel jackets. Then it was placed in an oven at 110 °C for 40 h. Final pH was about 11 when it was opened. The products were centrifuged and washed repeatedly with deionized water, then dried in 70 °C, and finally 1.2 g of crystal sample was obtained. As a starting material zinc carbonate hydroxide as well as hydrozincite, $(\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6)$ was used instead of LDH for comparison.

2.2 Characterization

The chemical analyses were carried out with inductively coupled plasma, ICP, (Seiko Instrument Inc., SPS4000) for metallic elements and phosphorus, and thermogravimetry, TG (Shimadzu, DT-40), for H_2O . Fourier transformed infrared, FT-IR, measurement was carried out with a Perkin-Elmer model 1640. Samples were pelletized with KBr powder. Powder X-ray diffraction, XRD, data were collected on a Rigaku RAD-C with $\text{Cu K}\alpha$ radiation filtered with Ni between $2\theta = 20^\circ$ and 80° in 0.02° steps. Rietveld refinement was carried out using the program RIETAN⁽⁷⁾ on an IBM RS/6000 computer. TG curves were recorded by heating from room temperature to 500 °C at a rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Differential scanning calorimetry, DSC, measurement was performed by a Shimadzu DSC-50 under the same

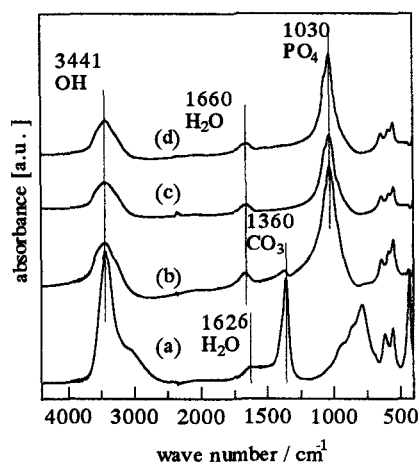


Fig.1 FT-IR spectra of (a) original Zn/Al-CO₃-LDH and products used with (b) Zn/Al-CO₃-LDH, (c) Zn/Ga-CO₃-LDH and (d) hydrozincite.

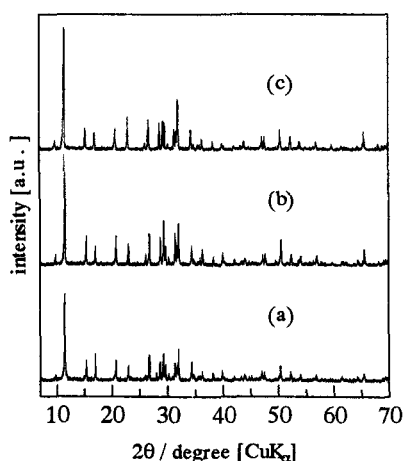


Fig.2 XRD patterns of the products used with (a) Zn/Al-CO₃-LDH, (b) Zn/Ga-CO₃-LDH and (c) hydrozincite.

conditions except using N₂ gas flow. Particle sizes were measured by laser diffraction particle size analyzer (Shimadzu SLAD-1100).

3. RESULTS AND DISCUSSION

3.1 Conversion of Zinc-containing LDH to CZP

Figure 1 shows the IR spectra obtained for the original Zn/Al-CO₃-LDH and the products. The spectrum of the LDH includes a strong OH stretching band centered at 3441 cm⁻¹, a weak H₂O bending band at 1626 cm⁻¹ and a strong CO₃²⁻ ν₃ stretching band at 1360 cm⁻¹. On the other hand, the OH stretching band and CO₃²⁻ ν₃ band are clearly weakened or eliminated in the case of the products. A strong adsorption at 1030 cm⁻¹ can be assigned to the PO₄³⁻ ν₃ stretching. These spectral changes confirm the conversion from carbonate salt to phosphate ones.

Figure 2 shows the XRD patterns obtained for the products. These XRD patterns of the products are quite similar to that of NaZnPO₄·H₂O.⁽²⁾ These reflections

Table I. Results of chemical analysis for the products

	Zn	Na	P	Al	Ga	H ₂ O
starting materials						
Zn/Al-CO ₃ -LDH	1.00	0.94	0.98	0.01	—	1.32
Zn/Ga-CO ₃ -LDH	1.00	1.00	1.06	—	0.00	1.54
Zn ₃ (CO ₃) ₂ (OH) ₆	1.00	1.01	0.98	—	—	1.57

The values are presented as the molar ratio to Zn.

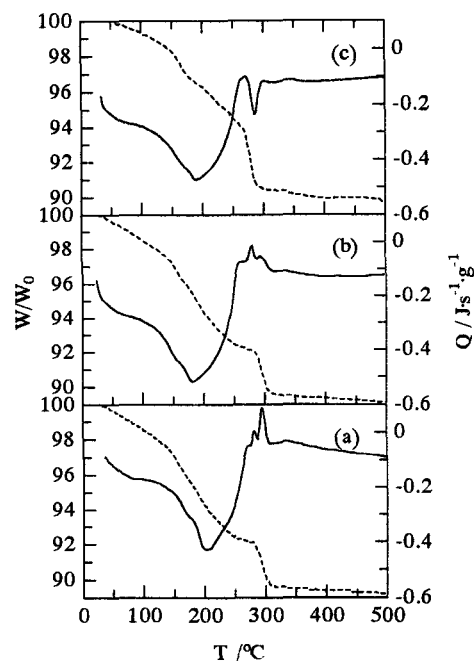


Fig.3 TG and DSC profiles of the products used with (a) Zn/Al-CO₃-LDH, (b) Zn/Ga-CO₃-LDH and (c) hydrozincite. TG: dashed line, DSC: solid line

were found to be indexed with hexagonal unit cell and its space group was suggested by extinction rule (000l, l≠6n) to be P6₁, P6₅, P6₁22 or P6₅22. These all space groups assigned helical structures. Thus, it was suggested that the products have a chiral framework.

The result of chemical analysis is presented in Table I. From this table, the conversion from carbonate salt into phosphate one is evidenced. Almost all of the Al³⁺ and Ga³⁺ ions in the LDHs were released from the solid phase; instead, Na⁺ ions were incorporated in the solid phase. The composition of the solid can be represented as a formula NaZnPO₄·nH₂O (n: 1.3~1.6).

Figure 3 shows TG and DSC profiles obtained for the products. For all the products, weight loss of about 11% occurred from room temperature to 300 °C, and no further weight loss until 500 °C. The DSC profiles of the products exhibited broad endothermic peaks from room temperature to 300 °C, associated with the weight loss at the identical temperature region of the TG. The weight loss can be assigned to the desorption of water

molecules in the products. At temperatures around 300 °C, however, the difference was observed in DSC profiles. The products from LDHs as starting materials exhibited exothermic peaks at 300 °C whereas the product from hydrozincite as a starting material exhibited endothermic peak at the same temperature. In this temperature, the CZP phase transformed through final dehydration to monoclinic NaZnPO₄.⁽⁸⁾ Thus, this transition process contains two opposite thermal processes, namely, the exothermic one due to the phase transition CZP to NaZnPO₄, and the endothermic one due to dehydration. It is noteworthy that the weight losses at this temperature are different each other. The product from hydrozincite as a starting material gave a larger weight loss as compared with the others. Consequently, the larger heat of dehydration involved in the transition of the product from hydrozincite as a starting material is considered to have hidden the exothermic process in the DSC profile.

3.2 Rietveld Refinement of Products

Rietveld refinement was carried out for the product from Zn/Ga-CO₃-LDH as a starting material. We started Rietveld refinement with Harrison's positional parameters⁽²⁾ for atoms in the unit cell. The positions and occupancies of framework atoms were fixed, but those for the Na⁺ and H₂O were parametrically optimized. The final cycle of the least squares converged to give residuals of R_{wp} (weighted pattern R-factor) = 9.40 %, R_p (pattern R-factor) = 7.31 % and R_F (structure factor R-factor) = 2.99 %. These relatively low values confirm that the structure of the product can be explained as the Harrison's structural model. Crystallographic details are summarized in Table II and III. The obtained model of the framework is drawn in Figure 4. The stoichiometry for Na⁺ and H₂O were very close to those from chemical analysis. The cell constants were calculated and found very close to Harrison's crystal (I). This result confirms the conversion from LDH to CZP.

3.3 Size and Morphology of the crystal

As a feature of this conversion process, we have found that the sizes of the produced crystal are strongly affected by the starting state of the suspension of the solid, that is, pretreatment conditions before setting the reaction jacket into the oven. When the starting aqueous phosphate suspension of Zn/Al-CO₃-LDH was stirred at room temperature for long time., e.g. 10 h, small crystals of size in the order of 10⁻⁶ m were obtained. On the other hand, when the time of the stirring was shortened, e.g. 1 h, the crystal size increased to the order of 10⁻⁵ m. In Table IV, the mean and maximum sizes of the particle with various period of the pre-stirring are presented. The reaction time of the hydrothermal conversion was fixed

Table II. Crystallographic data for the product of the product used with Zn/Ga-CO₃-LDH

Wavelength	0.15418 nm
Profile range	15-70°
Step scan increment	0.02
Space group	P6 ₁ 22 (178)
a	1.04730(4) nm
c	1.50631(4) nm
Number of observations	2749
Number of reflections	159
Number of profile parameters	6
Number of structural parameters	31
R_{wp}	9.40%
R_p	7.31%
R_F	2.99%

Table III. Atomic positional parameters and isotropic thermal parameters (Å²) of the product used with Zn/Ga-CO₃-LDH

Atom	Site	x	y	z	g	B(Å ²)
Na1	6b	0.72(2)	0.4484	0.25	0.15(8)	4(2)
Na2	12c	0.620(6)	0.334(7)	0.248(6)	0.49(5)	
Zn1	6b	0.8414	0.6827	0.25	1	1.4(2)
Zn2	12c	0.5071	0.4929	0.41667		
P	12c	0.8324	0.5912	0.4409		2.4(6)
O1	12c	0.805	0.5403	0.3439		
O2	12c	1.0485	0.8019	0.2185		
O3	12c	0.689	0.571	0.4808		
O4	12c	0.873	0.489	0.491		
O-1	12c	0.28(1)	-0.61(1)	-2.39(1)	0.29(5)	14(3)
O-2	12c	0.43(2)	0.40(1)	0.206(9)	0.37(5)	
O-3	12c	0.044(6)	-0.085(7)	-0.010(5)	0.71(9)	
O-4	12c	0.410(7)	0.26(1)	0.124(5)	0.65(6)	

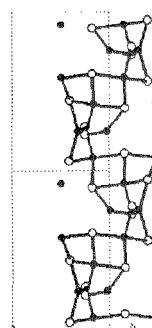


Fig.4 Framework model obtained from refinement. Framework oxygen omitted

Table IV. Relation between particle size and stirred time before hydrothermal reaction

Stirred time (h)	particle size (μm)	
	mean	
0	36.1	
1	32.8	
5	7.8	
10	3.9	

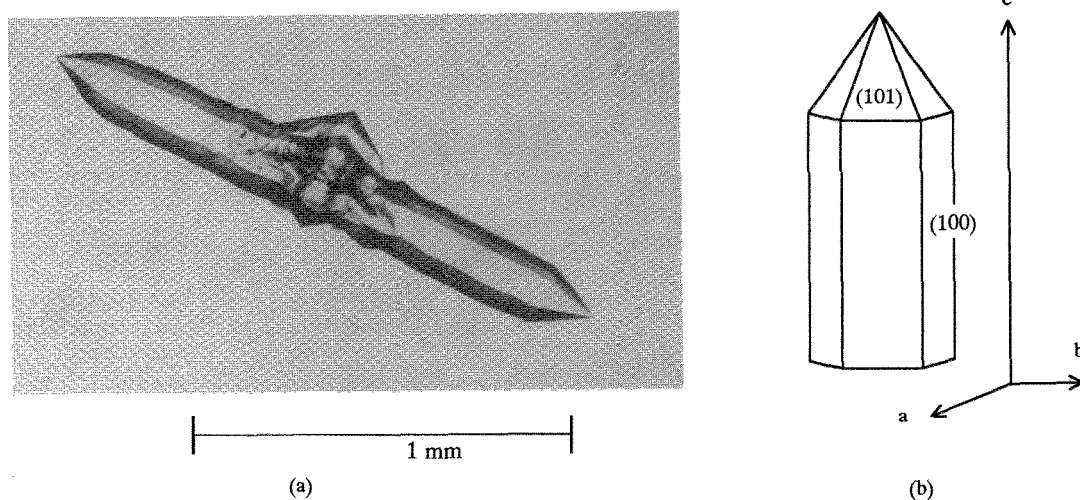


Fig.5 Optical micrograph (a) of CZP crystal which prepared with the procedure in section 3.3 and a schematic crystal model of the product (b).

to be 40 h for all cases. From this table, we can find a tendency that longer pre-stirring time gives smaller size of the particle.

This result suggested strongly that the pre-processing of the suspension could have a crucial rule in modification of the crystal size of CZP. Through several trials and errors, we finally obtained a considerably large CZP crystal with dimension of $0.2 \text{ mm} \times 0.2 \text{ mm} \times 1.0 \text{ mm}$ in morphology of capped hexagonal rod as shown in Figure 5(a). Most of the well-grown crystals showed facets of (101) and (100) planes of the CZP structure as shown Figure 5(b). This result suggests that the crystals grow mainly along c-axis.

The conditions used for this reaction are as follows: (1) the aqueous suspension of Zn/Al- CO_3 -LDH without phosphate ions were agitated by supersonic wave irradiation for 1 h; (2) the suspension was mixed with Na_2HPO_4 aqueous solution of concentration of 3 times as much as that described above; (3) this suspension was carefully but quickly moved into the bomb reactor, and followed by the same procedure described above. A rational understanding on the relation between the crystal growth and the initial state of the suspension has not been obtained yet. However, well-grown crystals of CZP have been reproduced by the same procedure at least 10 times so far.

4. CONCLUSION

Conversion of zinc-containing LDH to CZP has been investigated under hydrothermal conditions in aqueous suspension system with sodium hydrogen phosphate. The chiral phase was successfully obtained under conditions at 110°C and pH 11 for all used LDHs. About 40 hours were required for complete conversion

to CZP.

To our knowledge, the crystal obtained here is the largest example of chiral microporous crystals. Further studies of the conversion of LDH materials to zincophosphate zeolites involved here should increase our understanding of crystal growth in zeolite synthesis. In addition, the relatively large chiral crystal with micropores could offer a starting step for exciting applications, such as stereoselective separation or microelectric or optoelectric devices.

ACKNOWLEDGEMENT

The ICP measurements and particle size analyses were performed in Akita Industrial Research Institute.

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(Received December 10, 1998; accepted April 14, 1999)