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Formation of Sodalite-Like Zincophosphate Framework from Zn/Al-Layered Double Hydroxide as a Starting Material

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The reaction between Zn/Al-layered double hydroxide (LDH) carbonate and Na_2HPO_4 in a suspension system was investigated under mild hydrothermal conditions. A sodalite-type sodium zincophosphate which incorporated a small amount of Al atoms was obtained at $pH = 10.0$, $T = 358$ K, under atmospheric pressure. The reaction was found to be sensitive to the reaction conditions. The obtained sodalite-like compound was characterized with FT-IR, powder XRD with Rietveld Refinement and thermal analyses. The product has a quite similar structure to that of the pure sodalite-like sodium zincophosphate, but showed an improved thermal stability compared to that of the pure one without Al.

Layered double hydroxides (hereafter we will use the abbreviation LDH) have been used as anion exchanger, precursors for mixed metal oxide with high surface area as well as for many kinds of intercalation compounds including pillared porous materials. The structure of these materials consists of brucite-like mixed cation double hydroxide layers with permanent positive charge and hydrated anion layers, alternating one on the other. The most popular compound of this family is hydrotalcite, which is constructed of Mg/Al hydroxide layers and carbonate anions as well as water molecules in the interlayer space.[1] The general chemical formula of these materials can be described as $M^{2+}_{1-x}M^{3+}_{x}(OH)_2A^{m-}_{x/m}\cdot nH_2O$, where A stands for interlayer anions with a valence of m.[2] It has been known that many kinds of cations can be accommodated in the brucite layer: e.g., Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} as divalent cations, and Al^{3+}, Ga^{3+}, Cr^{3+}, Fe^{3+} as trivalent ones. It should be noted that most of these cations could also be accommodated in the framework of the zeolite-like structure.

Zeolites are well-known cation exchangers with micropores in the structure. They are constructed from TO_4 tetrahedra (T = tetrahedral atom); the O atoms are shared between two adjacent tetrahedra giving a framework ratio $O/T = 2$. Although a zeolite is an aluminosilicate in a narrow sense, many types of substitution in the framework with T atoms other than Si and Al have been performed in the field of synthesis of zeolites. Such substitution is considered to be effective for modification in the structure and physico-chemical properties of the framework.[3] From the fact that the LDHs contain these hetero atoms, we considered that the possibility of conversion from LDH to zeolite should be investigated to extend the knowledge of zeolite formation. Recently, Stucky and co-workers have synthesized a number of new zincophosphates including new types of structure in addition to zeolite analogues, e.g. sodalite and faujasite.[4,5] They prepared these materials even at room temperature. The fact that Zn–O–P linkage can be easily obtained under ambient conditions prompted us to study the formation of zinc-containing zeolite analogues from zinc-containing LDH as the first step of the study.

The purpose of this paper is to demonstrate the possibility of conversion from zinc-containing LDH to sodalite-type zincophosphate. For this purpose, we examined the reaction between Zn/Al-LDH carbonate and sodium hydrogen phosphate under mild hydrothermal conditions. The structure and thermal properties of the product will be presented.

Experimental

Reaction between Zn/Al-LDH and Sodium Hydrogen Phosphate. Zn/Al-LDH powder, $Zn_2Al(OH)_6(CO_3)_{0.5}\cdot 1.5H_2O$ was prepared with the conventional coprecipitation method.[6] The structure of the LDH was found to be characterized in space group of $R\bar{3}m$ with $a = 306.8$ and $c = 2267$ pm. The LDH powder of 1.0 g was dispersed in 400 cm^3 of 0.1 $mol\,dm^{-3}$ Na_2HPO_4 aqueous solution. The suspension was stirred with a magnetic stirrer and kept at 358 K under atmospheric pressure for 40 h. Throughout the reaction, the solid powder remained in the system; thus no transparent phase appeared even in the initial stage. The reaction was monitored by measuring the FT-IR spectra of intermediate states of powder. The progress of the reaction was observed by extinction of the IR absorption of carbonate vibration instead of appearance of that of phosphate. The product powder was separated centrifugally, washed repeatedly with deionized water, then dried in vacuo at 313 K, and finally 1.2 g of powder sample was obtained, which was soluble in acidic solution.

To clarify the effect of pH of the suspension on the reaction, we proceeded the same reactions with different pH values of the starting solutions by adding proper amounts of NaH_2PO_4 and NaOH under the conditions that the concentration of $PO_4{}^{3-}$ ions was kept constant.

Characterization. The chemical analyses of the starting LDH and the product were carried out with an ICP instrument (Seiko

Instrument Inc., SPS4000) for metals and phosphorus, gravimetry for H_2O, and GC for CO_2. A scanning electron-microscopic observation (SEM) as well as an energy dispersive X-ray microanalysis (EDX) were performed with Hitachi S-4500 electron microscope. FT-IR spectroscopic measurement was carried out with a Perkin–Elmer Spectrometer model 1640. The specimens were prepared by mixing and pelletizing 1.0 mg powdered sample with KBr in a 1 : 100 ratio. The powder X-ray diffraction data were collected on a Rigaku RAD-C diffractometer with Cu $K\alpha$ radiation filtered with Ni metal between $2\theta = 20°$ and 80° in 0.02° steps. Rietveld refinement was carried out using the program RIETAN[7] on an IBM RS/6000 computer. Thermogravimetric curves were recorded on a Shimadzu TG-40 thermobalance by heating from room temperature to 773 K at a rate of 5 $\mathrm{K\,min^{-1}}$ under a helium flow at a rate of 50 $\mathrm{cm^3\,min^{-1}}$. Differential scanning calorimetry was performed by a Shimadzu DSC-50 calorimeter under the same conditions except using nitrogen gas flow.

Results and Discussion

FT-IR Measurement. Figure 1 shows the spectra obtained for the original Zn/Al-LDH carbonate and the products with different reaction times. As can be seen, the spectrum of the LDH includes a strong OH stretching band centered at 3441 $\mathrm{cm^{-1}}$, a weak H_2O bending band at 1626 $\mathrm{cm^{-1}}$ and a strong $CO_3{}^{2-}$ ν_3 stretching band at 1363 $\mathrm{cm^{-1}}$. On the other hand, the OH stretching band and $CO_3{}^{2-}$ ν_3 band are apparently weakened or eliminated in the case of the products. These feature a strong absorption at 1033 and 1002 $\mathrm{cm^{-1}}$, which can be assigned to the $PO_4{}^{3-}$ ν_3 stretching. We can also see splitting absorption lines due to $PO_4{}^{3-}$ ν_4 vibration in the frequency region from 619 to 532 $\mathrm{cm^{-1}}$. These spectral changes confirm the conversion from carbonate salt to phosphate one.

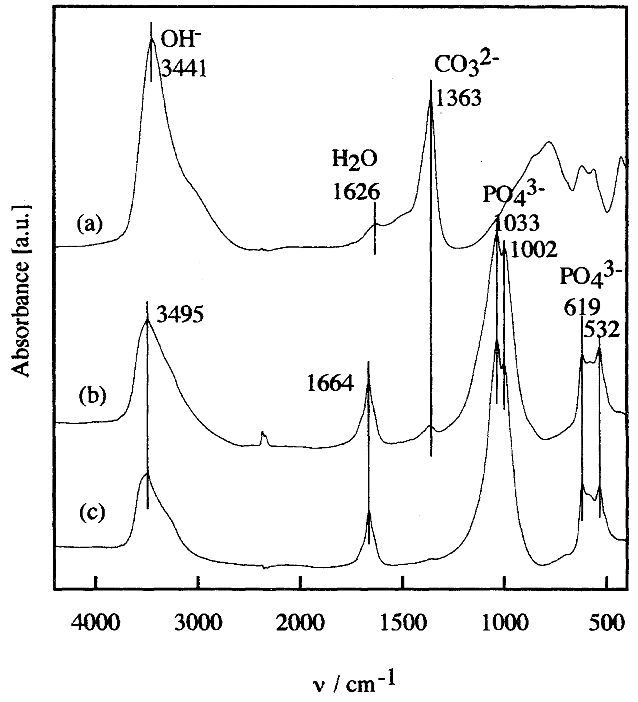

Fig. 1. FT-IR spectra of (a) original Zn/Al-LDH carbonate, and products with reaction time: (b) 20 h and (c) 40 h.

Chemical Composition and SEM Observation. The result of chemical analysis is presented in Table 1. From this table, the conversion from carbonate salt into phosphate one is also evidenced. Most of the Al^{3+} ions in the LDH were released from the solid phase; instead, a significant amount of Na^+ ions were incorporated in the solid phase. The chemical composition of the product is very close to that in the sodalite-type sodium zincophosphate, $Na_6(ZnPO_4)_6\cdot 8H_2O$, presented by Nenoff et al.[4] However, a small amount of Al^{3+} ions remained in the product. In addition, slight deviation of 1 or 2% in stoichiometry from the above formula can be also observed for the other species: Na, Zn, P, and H_2O.

To clarify the distribution of Al atoms in the product, a microscopic observation and elemental analysis by EDX were carried out. In Fig. 2, the SEM images of the starting LDH and the product are presented. It is obvious that the morphologies are different. There can be seen aggregation of hexagonal platelets for the LDH in Fig. 2a, whereas well-crystallized large particles with clear facets can be seen for the product in Fig. 2b. In the EDX microanalysis for the product particles, we detected Al $K\alpha$ signal from all of the particles, but the Al/Zn atomic ratio was much less than the value expected from the chemical formula of Zn/Al-LDH. From the data collected from 10 well-crystallized particles, we estimated the Al ratio to Zn as 0.04(2) for the product.

XRD Measurement and Rietveld Refinement. The XRD pattern of the product showed a primitive cubic framework ($a = 882.4$ pm) consistent with the extinction rule for space group $P\bar{4}3n$, which is quite similar to that of $Na_6(ZnPO_4)_6\cdot 8H_2O$ with sodalite-like framework reported by Nenoff et al.[4] Using this space group as well as the fraction coordinates for $Na_6(SiAlO_4)_6\cdot 8H_2O$ presented by Felche et al.,[8] we started Rietveld refinement procedure. The result of the refinement for the product is illustrated in Fig. 3, which includes the observed (dots in the upper part), calculated (line in the same part), and difference (dots in the bottom) profiles as well as the ORTEP (Oak Ridge Thermal Ellipsoid Plot) view of the sodalite β cage. The final cycle of the least squares converged to give residuals of R_{WP} (weighted pattern R-factor) = 13.5%, R_{P} (pattern R-factor) = 10.1% and

Table 1. Results of Chemical Analysis for the Starting LDH and the Product
The Values Are Presented as The Molar Ratio to Zn

Sample	Zn	Al	C	P	Na	H_2O
Zn/Al-LDH	1.0	0.50(2)[a]	0.25(2)	—	—	2.25(2)
Product	1.0	0.04(2)	Trace	1.01(2)	0.98(1)	1.41(2)

a) The values in parentheses represent the standard deviation.

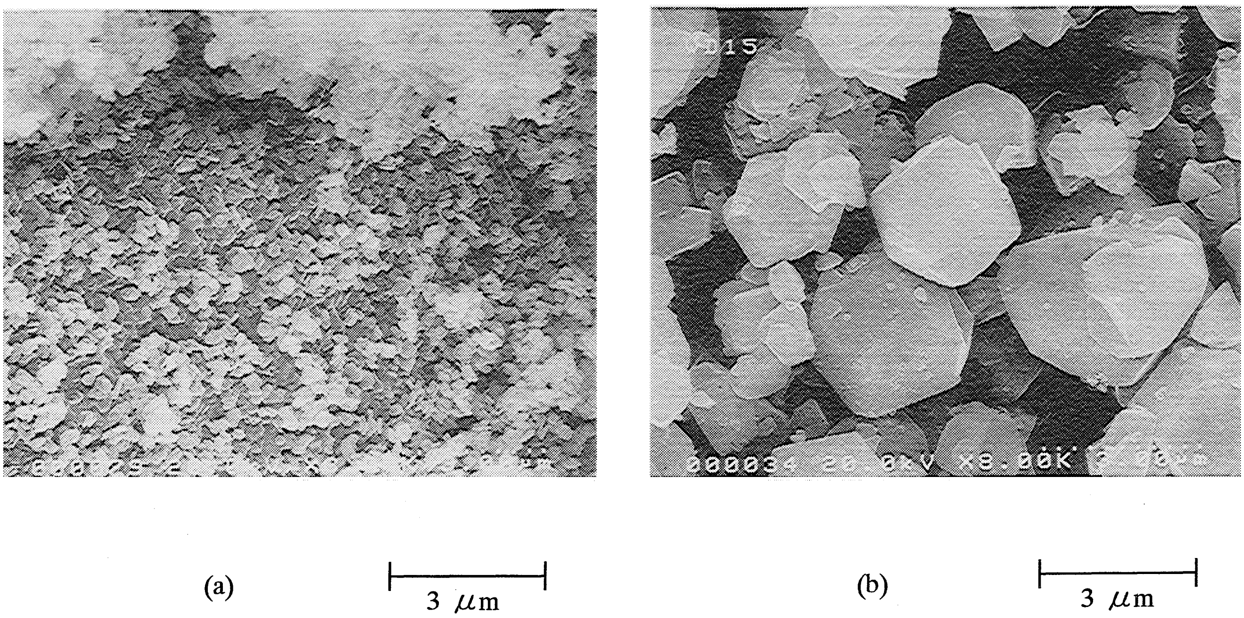

Fig. 2. SEM photographs of (a) the Zn/Al-LDH and (b) the product.

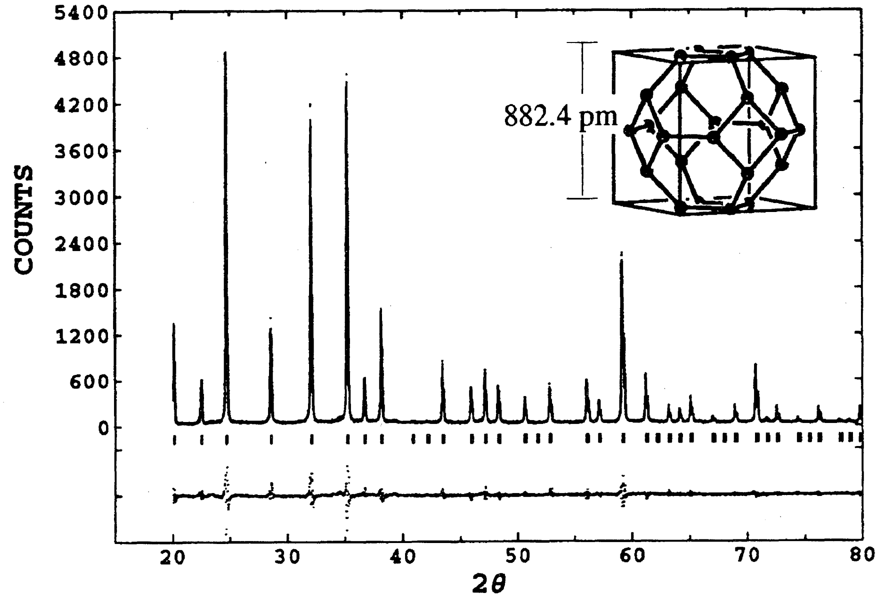

Fig. 3. Rietveld refinement result for the sodalite-type product and ORTEP view of β cage of Zn and P atoms reconstructed from refined parameters; O atoms are omitted for clarity.

R_F (structure factor R-factor) = 2.1%. These relatively low values confirm that the structure of the main product can be explained as the sodalite framework. Crystallographic details are summarized in Table 2, and final parameters in Table 3, and selected bond distances and angle in Table 4, in which the data for $Na_6(ZnPO_4)_6\cdot 8H_2O$ presented by Nenoff et al.[4] are also presented for comparison.

In sodalite-like structure, ZnO_4 and PO_4 units alternate with each other throughout the structure, forming a spherical cavity, β cage, in which a di-tetrahedral complex cation $[Na_3(H_2O)_4]^{3+}$ resides. Although there appears no relation in the structures between the LDH and sodalite structure, it is interesting that the distance between two diagonally facing hexagonal rings in a β cage ($=\sqrt{3}/2a$) is very close to the basal spacing of the LDH ($=c/3$). In our case, these values are 764 and 756 pm, respectively. In a heterogeneous suspension system, the initial nucleation would proceed on solid surface sites. In our case, we speculate that the edge sites of the LDH crystal may provide such nucleation sites. Under such a situation, it is likely that the array of stacked Zn/Al hydroxide sheets with interlayer spacing of 755 pm would provide geometrically favorable conditions on organizing the sodalite β cage.

The comparison in Table 4 hints at a similarity between these two sodalite-like structures, but slight differences can also be distinguished. In our sample, the bond length Zn–O is shorter, but on the contrary, P–O is longer than those of Nenoff's data. Although the differences are quite small, they

Table 2. Crystallographic Data for the Product

Data collection temp	298 K
Wavelength	154.18 pm
Profile range	20—80°
Step scan increment	0.02
Space group	$P\bar{4}3n$ (218)
a	882.47(1) pm
No. of observations	2999
No. of refrections	100
No. of profile parameters	6
No. of structural parameters	5
R_{wp}	13.50%
R_{p}	10.09%
R_{f}	2.14%

Table 3. Atomic Positional Parameters and Isotropic Thermal Parameters (Å^2)

Atom	Occupancy	x	y	z	B
Zn	1	0.25	0.5	0	1.6(2)
P	1	0.25	0	0.5	1.4(4)
O(1)	1	0.118(18)	0.413(2)	0.152(1)	1.4(7)
O(2)	1	0.368(3)	0.368(3)	0.368(3)	0.7(7)
Na	0.75	0.140(3)	0.140(3)	0.140(3)	4(1)

Table 4. Selected Bond Distance (Å) and Angle (deg) and Their esd's in Parenthese

	Product	Nenoff et al.[4)]
Zn–O(1)	1.93(18)	1.946(6)
P–O(1)	1.55 (14)	1.531(3)
Na–O(1)	2.41(3)	2.414(8)
Na–O(2)	2.40(2)	2.397(8)
Zn–O(1)–P	126(1.4)	126.1(3)

are considered to be out of experimental error. This result suggests that a small amount of Al atoms substitute at the Zn position. This is also supported by the difference in the lattice constant. Their value of a is 882.805(12) pm, whereas our value is 882.470(13) pm. Taking account of the ionic radii of Al^{3+} (=0.039 nm), Zn^{2+} (=0.060 nm) and P^{5+} (=0.017 nm),[9)] one can conclude that substitution by Al at Zn site causes reduction in the lattice constant.

Besides the Zn site, the P and Na sites as well as the body center position are also considered to become the substitution sites by Al atom. We also tried the Rietvelt refinement taking account of these substitutions by Al atoms. Among these substitutions, P site and the body center position substitutions gave poorer profile fitting. Even in the cases of Zn and Na sites, no better profile fitting was obtained exceeding 0.1% in R-factors. It was considered that the distribution of Al atoms in the structure can hardly be determined unambiguously only by Rietveld refinement in the present case.

From the viewpoint of charge density on the framework, a Zn–O–Al linkage as a result of Al-substitution at P site is unfavorable due to high negative charge. On the contrary, a P–O–Al linkage is favorable due to neutralization of local charge. When an Al atom substitutes at a Zn site, the negative charge of the $\mathrm{ZnPO_4}$-framework is reduced by unity, and the charge balance of the structure would be attained by making a Na^+ site vacant. Consequently, we deduced the most probable conclusion that the chemical formula can be presented as $\mathrm{Na}_{6(1-\delta)}[(\mathrm{Zn}_{1-\delta}\mathrm{Al}_{\delta})\mathrm{PO_4}]_6\cdot 8\mathrm{H_2O}$. Gathering the results described above, we estimated the value of δ to be 0.04(2).

Thermal Decomposition Property. As can be seen in Fig. 4, the product exhibits a very sharp endothermic peak at 518.6 K, associated with a weight loss at the identical temperature region. The observed 11.8% weight loss can be assigned to the desorption of water molecules in the β cage. On the basis of the stoichiometric compound, $\mathrm{Na_6(ZnPO_4)_6\cdot 8H_2O}$, we can expect a weight loss of 11.6%. If we take account of the nonstoichiometry mentioned above, the loss should increase as δ-value increases. This is consistent with the result.

It is noteworthy that the dehydration temperature is higher than that reported by Nenoff et al.[4)] They reported that the dehydration occurs at 413 K and continues up to 473 K. The dehydration at these relatively low temperatures was reproduced for the sample prepared by us after Nenoff's method. In addition, they also reported the occurrence of an intermediate hexagonal phase between sodalite-type phase and unhydrous $\mathrm{NaZnPO_4}$ phase. However, our own sample gives no such hexagonal phase during the transition. The improvement in thermal stability is considered to be important from a practical viewpoint. Generally speaking, the thermal properties of zeolite materials vary depending on the crystallinity, the concentration of defects or hetero atoms as well as the kind of the extraframe cations. Although the observed difference seems to be associated with the coexistence of Al^{3+} ions in our sample, further study on the detailed structure of the sample is needed to understand its thermal properties.

Consideration on Reaction Conditions. The reaction was found to be quite sensitive to the pH value of the

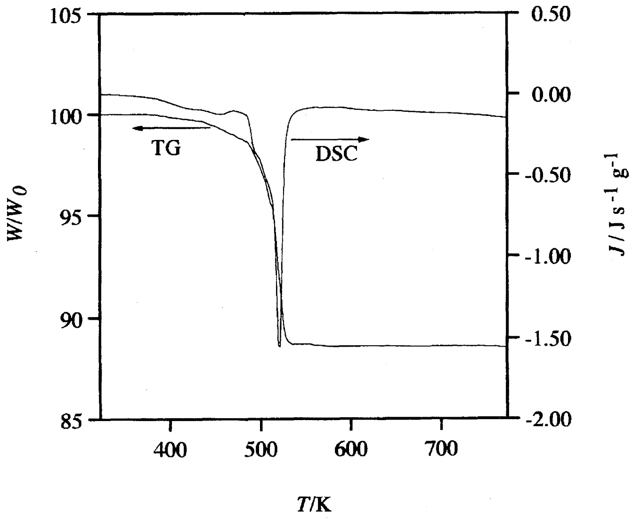

Fig. 4. Thermogravimetric curves (TG) and differential scanning calorimetric curves (DSC) for the sodalite-type product.

suspension. When the pH was less than 9.0, the reaction was not significantly proceeded, with the starting LDH remaining unreacted. On the other hand, when the pH was higher than 10.0, some other phase coexisted with sodalite-like phase. The XRD pattern of the by-product which appeared in the higher pH region was quite similar to that of $Na_3Zn_4O(PO_4)_3\cdot 6H_2O$ (S.G. $= R3c$; $a = 1074.89(3)$ pm, $\alpha = 60.114(2)°$) reported by Harrion et al.[11)] The conversion from LDH into a sodalite-like structure was exclusively observed in the pH region between 9.0 and 10.0. There was a tendency that the ratio of the sodalite-like phase to the LDH increased as the pH increased. The reaction was also found to be sensitive to the temperature. The sodalite-like phase was obtained below 363 K. Under the boiling conditions, a hexagonal phase was obtained whose XRD pattern was quite similar to a chiral hexagonal phase (S.G. $= P6_122$; $a = 1047.9$ pm, $c = 1509.8$ pm) reported by Harrison et al.[10)] From these results, we concluded that the optimum conditions to give sodalite-like phase are restricted in a narrow pH region close to 10.0 as well as at temperatures around 358 K.

The pH region where the sodalite-like phase was obtained is different from that for the pure sodium zincophosphate. Harrison et al. reported that the structure of the sodium zincophosphates is sensitive to the pH of the preparation suspension.[11)] According to them, a sodalite-like phase is obtained in the pH region between 6 and 8, and a cubic semi-dense phase (Cubic, $a = 1193.8$ pm) is obtained in the pH 10. The structure of the zeolite-like compound varies depending on pH, temperature, concentration and other synthetic conditions, so it is difficult to explain this pH difference simply. However, the difference in the pH region where sodalite-like phase is obtained may be attributed to the coexistence of Al^{3+} ions both in the solution and solid phases in our case.

Recently, Depege et al. have reported a condensation reaction between hydroxide sheets of LDH and silanols introduced into the interlayer space, giving rise to a nano-composite with layered clay structure.[12)] However, in our case, we have not yet obtained any clear evidence for intercalation of phosphate ions into the interlayer space; moreover, the layered character in morphology of the original LDH was completely lost in the product, as shown in Fig. 2. Therefore, it is difficult to describe the conversion process from LDH to sodalite-like phase by such a topochemical scheme. While the solution phase seems to play more important role in our process, the detailed mechanism is still unknown, open to future investigation.

Conclusion

Conversion from Zn/Al-LDH carbonate to sodalite-like zincophosphate proceeded at 358 K under atmospheric pressure through the reaction with sodium mono-hydrogen phosphate aqueous solution. The product in sodalite-like structure was quite similar to $Na_6(ZnPO_4)_6\cdot 8H_2O$, but with a small amount of Al atoms incorporated into the structure. The thermal stability of the structure was higher than that of pure sodalite-like sodium zincophosphate.

The present result seems to add an extension to the knowledge of the reactivity of zinc-containing LDH. The LDH has been considered to be stable under the pH conditions used in this study. However, phosphate ions can attack the brucite-like hydroxide sheet easily, causing a rearrangement of the atoms to form a 3-dimensional framework even under mild hydrothermal conditions.

Although a sodalite structure itself is dense with no open pore accessible for molecules, the β cage takes a major part in forming open frameworks such as faujasite. In addition, many zincophosphates with new open pore structures have been recently synthesized.[10,11)] The Al-incorporation into the sodalite-like structure suggested here seems interesting from the viewpoint of modification of properties of this group of materials. The present result suggests a possibility of incorporation of the third element into the zincophosphate zeolite-like framework.

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