A Solvent-free Synthesis of Zn–Al Layered Double Hydroxides

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(Received December 12, 2006; CL-061455; E-mail: a.sonoda@aist.go.jp)

We have demonstrated for the first time a solvent-free synthesis of Zn–Al layered double hydroxides, Zn–Al LDH(Cl), by grinding solid ZnO and $AlCl_3 \cdot 6H_2O$ and then by autoclaving at 150 °C for 1 day without the addition of water and alkaline solution.

Synthetic hydrotalcite-like materials, also known as layered double hydroxides (LDH), have a general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}$ $[(A^{m-})_{x/m} \cdot nH_2O]^{x-}$, which is denoted as M_1M_2–LDH(A), where the brucite-type layers have $M_1{}^{2+}$ cations (Mg, Zn, Cu, Co, and Ca) and the $M_2{}^{3+}$ cations (Al and Fe) at the octahedral centers, and anions, A^{m-}, such as $CO_3{}^{2-}$, Cl^-, or $NO_3{}^-$, are occupied between the layers to balance the charge. A variety of LDHs materials has been synthesized for their applications.[1–5] Interestingly, Zn–Al LDH(Cl) materials have been studied as hosts for incorporation of amino acids and DNA in the interlayer.[6,7]

There have been a number of methods for synthesis of Zn–Al LDH materials; a coprecipitation method at constant pH,[1] a urea method,[8] and a reconstruction method.[9,10] Recently, Zn–Al LDH(Cl) has been synthesized by a biomineralization process,[11] which also causes the contamination of carbon dioxide in the material. The synthesis of Zn–Al LDH(Cl) by the conventional coprecipitation method involves the addition of alkaline solution to control pH.[1]

We have succeeded the solvent-free synthesis of Zn–Al LDH(Cl) among several explored systems of M_1–M_2 pairs. This study is the first demonstration of the solvent-free synthesis of Zn–Al LDH(Cl). The phosphate uptake of the resultant material is also described.

ZnO (2 g) and $AlCl_3 \cdot 6H_2O$ (2–3 g) (Wako Chemicals, Japan) were mixed in Zn/Al molar ratios of 2 and 3, ground, and autoclaved at 150 °C in a Teflon-lined stainless steel vessels (50 cm^3) for 1 day. After cooling to room temperature, the solid materials were washed with deionized water, and air-dried. The resultant materials are abbreviated as ZnAl–LDH(Cl)-1 and ZnAl–LDH(Cl)-2 for the Zn/Al molar ratios of 2 and 3, respectively.

XRD patterns were recorded on a Rigaku type RINT 1200 X-ray diffractometer with a graphite monochromator with Cu Kα radiation ($\lambda = 0.15406$ nm). Chemical analysis of Zn and Al was carried out by using a Seiko SPS 7800 atomic emission plasma spectrometer. Chloride content was determined by ion chromatography. Carbon content was determined by a carbon analyzer, Horiba EMIA-U511.

Phosphate exchange was carried out by equilibrating ZnAl–LDH(Cl)-2 (0.05 g) with NaH_2PO_4 solution (50 cm^3) with different concentrations (5–90 mg-P/dm^3) at pH 5.5 for 3 days at room temperature. Phosphate concentration in solution phase was determined by persulfate UV oxidation method[12] using a portable colorimeter, Model DR/700, HACH Co., U.S.A.

The diffraction peaks of ZnO can be indexed to a hexagonal structure with lattice parameters of $a = 0.324$ nm and $c = 0.519$ nm. The formation of LDH phase was observed by measuring X-ray diffraction patterns of the products with different autoclave times (Figure 1). The formation of a well-crystallized LDH phase without any impurity is attained completely after 24 h. The Miller indexing in Figure 1 is referred to a rhomohedral ($R3m$) symmetry.[9] The calculated lattice parameters are $a = 0.308$ nm and $c = 2.338$ nm for ZnAl–LDH(Cl)-1 and $a = 0.308$ nm and $c = 2.344$ nm for ZnAl–LDH(Cl)-2. These values are in agreement with those reported for Zn–Al LDH prepared by a coprecipitation method[13] ($a = 0.308$ nm and $c = 2.355$ nm) and a urea method[14] ($a = 0.307$ nm and $c = 2.321$ nm).

SEM image of ZnAl–LDH(Cl)-2 shows the packed agglomerates of sheet-like particles with sizes around 1 µm.

Analysis data of ZnAl–LDH(Cl)-1 and -2 materials are given in Table 1. The Zn/Al molar ratios of 1.74 and 1.94 at 24 h are smaller than those in the starting mixtures; this difference is probably due to the uncompleted reaction of Zn^{2+} ions.

The formulae show that positively charged brucite layers are balanced by the negative charge of the anions present between the layers. The ratios $(Cl^- + 2CO_3{}^{2-})/Al^{3+}$ are 0.94 and 1.02 for ZnAl–LDH(Cl)-1 and -2, respectively, as expected for pure LDH. The ZnAl–LDH(Cl)-2 has a Zn/Al molar ratio close to 2, which is consistent with the ideal LDH formula $Zn_2Al(OH)_6(Cl) \cdot nH_2O$.

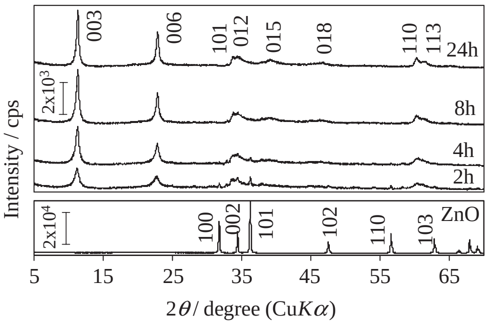

Figure 1. XRD patterns of ZnAl–LDH(Cl)-1 at different intervals of autoclave at 150 °C.

Table 1. Chemical compositions of Zn–Al LDH(Cl)

Material	Zn/Al[a]	Formula
ZnAl–LDH(Cl)-1	2 (1.74) (1.77)†	$[Zn_{0.61}Al_{0.35}(OH)_2][Cl_{0.31}$ $(CO_3)_{0.01} \cdot 0.78H_2O]$
ZnAl–LDH(Cl)-2	3 (1.94)	$[Zn_{0.66}Al_{0.34}(OH)_2][Cl_{0.34}$ $(CO_3)_{0.003} \cdot 0.86H_2O]$

[a]Molar ratio. The values in parenthesis denote resultant materials after 24 and 8 h†.

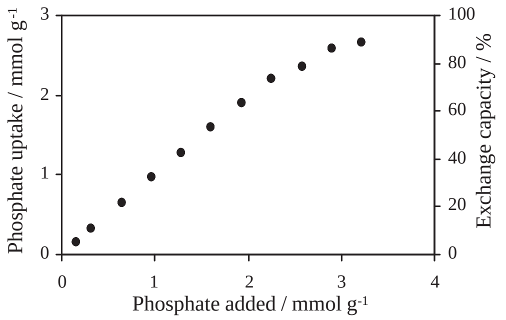

Figure 2. Phosphate uptake on ZnAl–LDH(Cl)-2. Weight, 0.05 g; Vol, 50 cm^3; Conc, 5–90 mg-P/dm^3; Contact time, 3 days; Equilibrium pH, 5.5.

Solvent-free reactions between ZnO and $AlCl_3 \cdot 6H_2O$ at 150 °C in a closed system to form a Zn–Al LDH can be expressed as follows:

$$AlCl_3 \cdot 6H_2O \rightarrow AlCl_3 + 6H_2O \tag{1}$$

$$ZnO + H_2O \rightarrow Zn(OH)_2 \rightarrow Zn^{2+} + 2OH^- \tag{2}$$

$$AlCl_3 + 3OH^- \rightarrow Al(OH)_3 + 3Cl^- \tag{3}$$

$$xZn^{2+} + Al(OH)_3 + (2x - 1)OH^- + yH_2O + Cl^- \rightarrow Zn_xAl(OH)_{2+2x}Cl^- \cdot yH_2O \tag{4}$$

Water vapor generated from $AlCl_3 \cdot 6H_2O$ reacts with basic ZnO particles to form $Zn(OH)_2$ on the oxide particle surfaces. The dissociation of $Zn(OH)_2$ releases Zn^{2+} and OH^- ions. OH^- ions react with $AlCl_3$ to form amorphous $Al(OH)_3$. The deposition of Zn^{2+}, Cl^-, and OH^- ions occurs on the surface of $Al(OH)_3$ particles, forming a pre-LDH to yield well crystallized LDH material in 1 day. Washing of the crude product with distilled water removes unreacted zinc ions.

The phosphate exchange on ZnAl–LDH(Cl)-2 was carried out at pH 5.5. At this pH, considerable phosphate species are $H_2PO_4^-$ (97%) and HPO_4^{2-} (3%), because of $pK_1 = 2.15$, $pK_2 = 7.20$, and $pK_3 = 12.33$ for phosphoric acid. The theoretical exchange capacity of the material is 3.0 mmol/g based on Cl^- content. The phosphate uptake (mmol/g) on the material is plotted with the mole of phosphate added (per the weight of the material mmol/g) in solution (Figure 2). The slope of the curve shows that almost all the added $H_2PO_4^-$ ions are exchanged with the Cl^- ions between the layers of the material, indicating high affinity for $H_2PO_4^-$ ions. The amount of $H_2PO_4^-$ ions exchanged reaches 88% of the theoretical exchange capacity.

XRD patterns of phosphate-exchanged ZnAl–LDH(Cl)-2 with increasing phosphate contents are shown in Figure 3. The original material ZnAl–LDH(Cl)-2 has an interlayer distance d_{003} of 0.78 nm with a layer thickness of 0.48 nm estimated from brucite.[1] For the 10% exchange with phosphate, although the XRD pattern is almost the same as that of the original material except for a slight decrease in crystallinity, and a new weak signal due to phosphate uptake appears at $2\theta = 7.8°$ ($d = 1.13$ nm). This signal is increased with a lower shift of 2θ when the phosphate exchange is increased. For more than 40% exchange with phosphate, the shifted (003), (006), and (009) signals due to the phosphate uptake become dominant, while the original (003) and (006) signals disappear completely for the 88% exchange. The shift of (00*l*) reflections to lower 2θ values indicates an increase in the interlayer distance. The (003) reflection corresponds to a d value of 1.18 nm ($2\theta = 7.5°$). The interlayer distance of 1.18 nm for the ZnAl–LDH(Cl)-2 with the 88% exchange is in agreement with the reported values for HPO_4^{2-} exchanged types of Zn–Al LDH(Cl) materials synthesized by other methods.[13,14] The broadness of (00*l*) reflections probably reflects a turbostratic disorder of the layers by the exchange of phosphate ions.

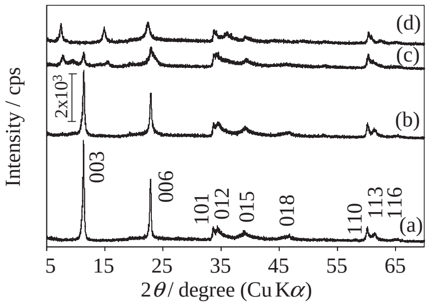

Figure 3. XRD patterns of (a) ZnAl–LDH(Cl)-2 and ZnAl–LDH(Cl)-2 with phosphate uptakes (b) 10%, (c) 40%, and (d) 88%.

In conclusion, a well crystalline Zn–Al LDH(Cl) material has been synthesized for the first time by a solvent-free synthesis. Phosphate exchange capacity at pH 5.5 is 2.6 mmol/g, which is 88% of the theoretical anion exchange capacity.

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Published on the web (Advance View) February 17, 2007; doi:10.1246/cl.2007.446