

## Preparation of $\text{PO}_4^{3-}$ , $\text{P}_2\text{O}_7^{4-}$ Anion-Pillared Nanocrystalline Mg-Al and Zn-Al Layered Double Hydroxides in Microwave Fields

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**Abstract:** Using nanocrystalline  $[\text{Mg-Al-CO}_3]$  and  $[\text{Zn-Al-CO}_3]$  as precursors,  $[\text{Mg-Al-PO}_4]$ ,  $[\text{Zn-Al-PO}_4]$ ,  $[\text{Mg-Al-P}_2\text{O}_7]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$  have been successfully synthesized by a direct reaction with the free  $\text{PO}_4^{3-}$  or  $\text{P}_2\text{O}_7^{4-}$  using the microwave techniques and the anion-exchange method. And the samples thus obtained were characterized by TEM, FT-IR and XRD. The results show that the initial interlayer carbonate ions can be completely replaced by the free  $\text{PO}_4^{3-}$  or  $\text{P}_2\text{O}_7^{4-}$  under controlled microwave conditions employed for a short time.

**Keywords:** Nanocrystalline, the anion-exchange method, microwave, layered double hydroxides.

The Mg-Al and Zn-Al layered double hydroxides (abbreviated as Mg-Al-LDHs and Zn-Al-LDHs) containing  $\text{PO}_4^{3-}$  or  $\text{P}_2\text{O}_7^{4-}$  as the interlayer anion (abbreviated as  $[\text{Mg-Al-PO}_4]$ ,  $[\text{Zn-Al-PO}_4]$ ,  $[\text{Mg-Al-P}_2\text{O}_7]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$ ) are usually prepared by  $\text{PO}_4^{3-}$  or  $\text{P}_2\text{O}_7^{4-}$  ion-exchange with the balancing interlayer anions, such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{OH}^-$ . However, in case of layered double hydroxides containing  $\text{CO}_3^{2-}$  as the interlayer anion,  $\text{CO}_3^{2-}$  is not readily replaceable by other anions, because the anion selectivity of hydrotalcite-like compounds is the highest for  $\text{CO}_3^{2-}$ . Now, using nanocrystalline Mg-Al and Zn-Al layered double hydroxides containing  $\text{CO}_3^{2-}$  (abbreviated as  $[\text{Mg-Al-CO}_3]$  and  $[\text{Zn-Al-CO}_3]$ ) as precursors,  $[\text{Mg-Al-PO}_4]$ ,  $[\text{Zn-Al-PO}_4]$ ,  $[\text{Mg-Al-P}_2\text{O}_7]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$  have been successfully synthesized by a direct reaction with the free  $\text{PO}_4^{3-}$  or  $\text{P}_2\text{O}_7^{4-}$  using the microwave techniques and the anion-exchange method for the first time.

### Experimental

The nanocrystalline  $[\text{Mg-Al-CO}_3]$  and  $[\text{Zn-Al-CO}_3]$  precursors had been synthesized according to the literatures<sup>2,3</sup>.

3.13 g (0.022 mol) of dibasic sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) was added to 50 mL of deionized water and stirred for 10 min so as to ensure a complete dissolution of the material. Then 5 g of the  $[\text{Mg-Al-CO}_3]$  precursor was added into the above solution and magnetic stirring was maintained for 5 min. The pH of this suspension was adjusted and

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monitored at 6.0 with a solution of HCl (0.5 mol/L) and continuously stirred for 30 min. Then the suspension was heated and refluxed at 90 °C for 10 min in a microwave field, then filtrated. The filter cake was washed free of excess phosphate ions by 250 mL deionized water at 40 °C. The product was then left to dry for 10 min in a microwave oven while the surface temperature of the product was maintained at 70 °C. 1.6 g of white [Mg-Al-PO<sub>4</sub>] crystals was obtained. 1.3 g of white [Zn-Al-PO<sub>4</sub>] crystals was synthesized with the same method using 5 g of [Zn-Al-CO<sub>3</sub>] as a precursor.

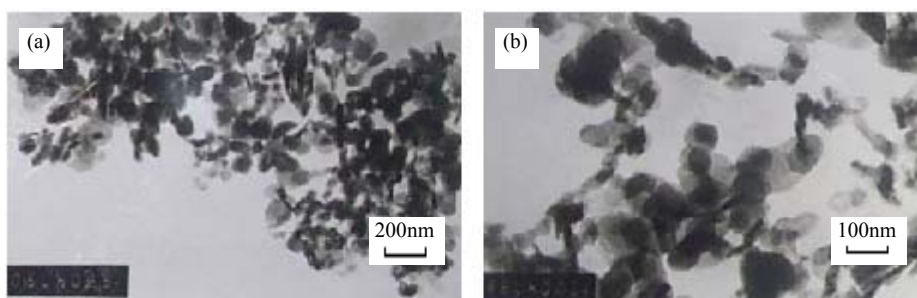
1.9 g of white [Mg-Al-P<sub>2</sub>O<sub>7</sub>] crystals was synthesized in the same way as that of [Mg-Al-PO<sub>4</sub>] from the [Mg-Al-CO<sub>3</sub>] precursor except that 8.3 g (0.019 mol) of sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>•10H<sub>2</sub>O) was used instead of dibasic sodium phosphate. 1.1 g of white [Zn-Al-P<sub>2</sub>O<sub>7</sub>] crystals was synthesized in the same way using 5 g of [Zn-Al-CO<sub>3</sub>] as the precursor.

## Results and Discussion

The size of [Mg-Al-CO<sub>3</sub>] and [Zn-Al-CO<sub>3</sub>] particles is about 10~50 nm and 10~60 nm, respectively, according to TEM pictures (**Figure 1**).

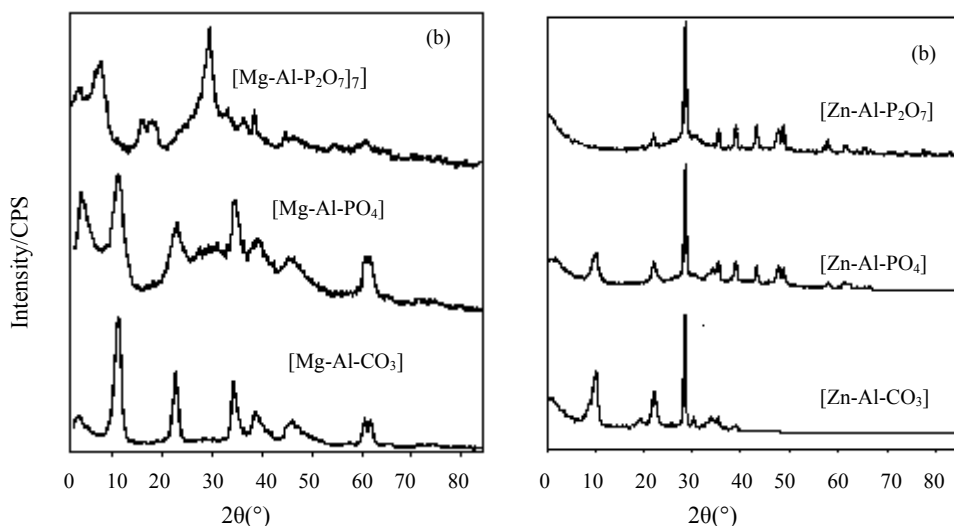
The IR data of Mg-Al-LDHs and Zn-Al-LDHs are shown in **Table 1**. From **Table 1**, we can see a marked difference between the products and the corresponding precursors in that the bands of the CO<sub>3</sub><sup>2-</sup> in the IR spectra of [Mg-Al-CO<sub>3</sub>] and [Zn-Al-CO<sub>3</sub>] are obvious while the bands of the CO<sub>3</sub><sup>2-</sup> in the IR spectra of [Mg-Al-PO<sub>4</sub>], [Zn-Al-PO<sub>4</sub>], [Mg-Al-P<sub>2</sub>O<sub>7</sub>] and [Zn-Al-P<sub>2</sub>O<sub>7</sub>] have entirely disappeared. This implies a highly efficient, stronger anion-exchange of PO<sub>4</sub><sup>3-</sup> or P<sub>2</sub>O<sub>7</sub><sup>4-</sup> with CO<sub>3</sub><sup>2-</sup> in a microwave field. The microwave

**Figure 1** TEM pictures of [Mg-Al-CO<sub>3</sub>] (a) and [Zn-Al-CO<sub>3</sub>] (b)



**Table 1** FT-IR absorption data and their attribution to the samples

Anion-pillared LDHs	v(P-O-P) (cm <sup>-1</sup> )	v(P=O) (cm <sup>-1</sup> )	v(P-O) (cm <sup>-1</sup> )	v(CO <sub>3</sub> <sup>2-</sup> ) (cm <sup>-1</sup> )	v(LDHs) (cm <sup>-1</sup> )
[Mg-Al-CO <sub>3</sub> ]	/	/	/	1381.8	659.3
[Mg-Al-PO <sub>4</sub> ]	/	1471.9	1069.2	/	650.7, 593.2
[Mg-Al-P <sub>2</sub> O <sub>7</sub> ]	908.0, 1119.4	1450.3	1047.8	/	566.5, 732.8
[Zn-Al-CO <sub>3</sub> ]	/	/	/	1384.1	574.1, 713.1, 875.1
[Zn-Al-PO <sub>4</sub> ]	/	1464.4	1068.7	/	572.0, 712.6, 874.9
[Zn-Al-P <sub>2</sub> O <sub>7</sub> ]	925.2, 1144.8	1462.3	1038.4	/	563.3, 713.6, 874.7

**Figure 2** XRD patterns of Mg-Al-LDHs (a) and Zn-Al-LDHs (b)

method can destroy the acting force between lamellar structures so that phosphate ions or pyrophosphate ions can easily exchange carbonate ions between the lamellar structures to be typical of hydrotacite-like materials<sup>4</sup>.

From **Figure 2 (a)** we can see that the exchanged materials including  $[\text{Mg-Al-PO}_4]$  and  $[\text{Mg-Al-P}_2\text{O}_7]$  tend to give relatively broader peaks while the parent carbonate precursor exhibits fine and intense peaks. This has often been assigned to a disturbance in the structure. Indeed, sometimes anions adsorbed on the surface will cause a default in the stacking sequence of the brucite-like sheets and a more disordered phase is generally expected to appear after the exchange process. But in the cases of  $[\text{Zn-Al-CO}_3]$ ,  $[\text{Zn-Al-PO}_4]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$  this phenomenon did not occur. From **Figure 2 (b)** we can see that  $[\text{Zn-Al-CO}_3]$ ,  $[\text{Zn-Al-PO}_4]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$  exhibit fine and intense peaks, characteristic of well-crystallised layered double hydroxides without exception. But they have also some differences. At  $2\theta=11.6^\circ$   $[\text{Zn-Al-CO}_3]$  has an apparent characteristic peak while the peak of  $[\text{Zn-Al-PO}_4]$  becomes weaker and the peak of  $[\text{Zn-Al-P}_2\text{O}_7]$  has entirely disappeared. However, at  $2\theta=47.6^\circ$  and  $48.5^\circ$  the new characteristic peaks of  $[\text{Zn-Al-PO}_4]$  and  $[\text{Zn-Al-P}_2\text{O}_7]$  appear. These facts also show that the exchangeable reactions have been successfully completed<sup>5</sup>. The differences of these XRD patterns can be explained by strong interactions existing between the anion and the brucite-type sheets through a so-called grafting process in a microwave field.

Therefore, the microwave method can not only make the exchange reaction possible but also shorten the interaction time dramatically to obtain the good crystal shape and crystallinity of the products.

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