Chinese Chemical Letters Vol. 15, No. 1, pp 90– 92 , 2004
http://www.imm.ac.cn/journal/ccl.html

Urea Decomposition Method to Synthesize Hydrotalcites

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Abstract: The urea decomposition property at high temperature has been used to control the pH value in the synthesis of layer compounds. The hydrotalcites of Mg-Al and Ni-Al with high crystallinity were synthesized by using this property.

Keywords: Hydrotalcite-like compound, urea decomposition, control of pH value.

Synthetic hydrotalcite-like compounds (HTlcs), categorical anionic clays which contain positively charged brucite-like layers, have recently attracted much attention due to the wide applications in many aspects[1, 2].

So far three methods have been used to synthesize the anionic clay[1]: titration coprecipitation, anionic exchange and thermal decomposition-reconstitution methods. Titration coprecipitation method includes low supersaturation and high supersaturation methods, respectively. The common drawback of the methods is that the instantaneous pH value is certainly different in different part of the slurry no matter how to increase the stirring speed. Although it is easier to crystallize in the low supersaturaion condition, which usually gives rise to precipitation, than in the high supersaturation condition in which the rate of nucleation is higher than that of crystal growth, it is still difficult to obtain the hydrotalcites with high crystallinity[1].

In order to overcome this shortcoming brought by titration coprecipitation process, a new method named homogeneous coprecipitation by urea decomposition was investigated, which may become a substitution. At low temperature urea can form a homogeneous solution with metal nitrates owing to its high stability. Raising the temperature of the solution up to 90°C, urea begins to decompose slowly and then the pH value of the solution increases subsequently. This process can sustain the pH value in every part of the solution to stay under a homogeneous level. Therefore, the hydrotalcites of Mg-Al, Zn-Al and Ni-Al with high crystallinity can be synthesized with this method.

Figure 1 shows the XRD patterns of Mg-Al, Zn-Al and Ni-Al hydrotalcites synthesized with different methods. It can be seen from the **Figure 1**, some general fe-

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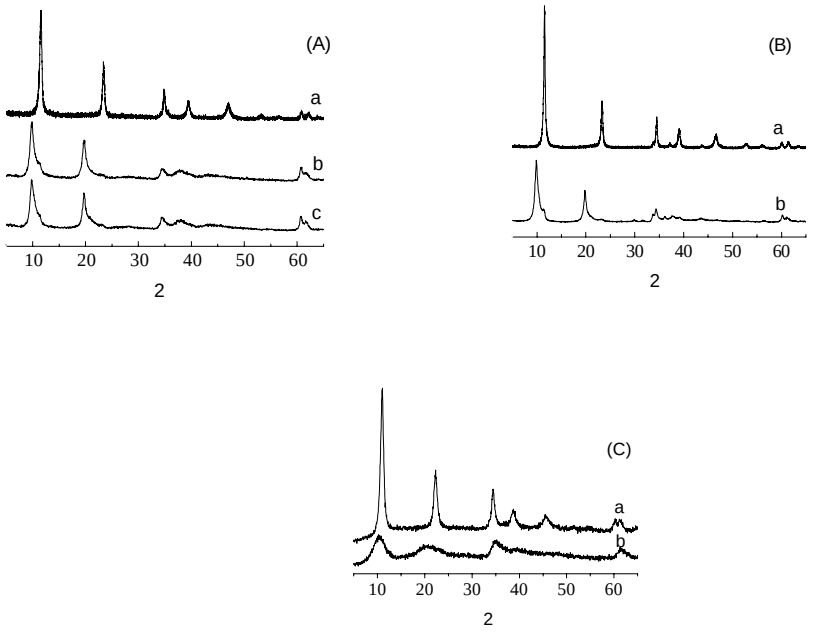
Figure 1 XRD patterns of Mg-Al (A), Zn-Al (B) and Ni-Al (C) HTlcs synthesized by using different methods.



(a) Urea method (urea/NO_3^- = 3, molar ratio); (b) Low supersaturation; (c) High supersaturation.

atures of HTlcs have observed with titration coprecipitation methods (**Figure 1** (A) (a) and (b), (B) (b) and (C) (a)). However, the relatively low intensities, broad peaks and asymmetric characteristics appear for the sample prepared by titration coprecipitation methods. These results indicate that disorder may be present in the stacking of the layers and the poor crystallinity is formed in these materials. However, the peaks of HTlcs prepared by urea method are narrow and sharp, as well as excellently symmetric. These phenomena suggest that the higher cyrstallinity and regular degrees exist in the structure of the layered materials.

Analyzing the position of the characteristic peaks of the HTlcs shown in **Figure 1**, it can be found that the positions of 003 and 006 reflections moved obviously to higher 2 θ values in the case of the samples prepared by urea method. The results imply that the interlayer region in the HTlcs samples synthesized with this method maybe lower than that in the samples obtained by titration coprecipitation methods. TG-DTA results have already proved that the water content in the samples synthesized with urea method is similar to that in other samples. Therefore, the influence of hydration degree can be ruled out. The difference of the interlayer region between the hydrotalcites samples synthesized by urea and titration methods is only due to the factor of the gallery anions. But if some salt of nitrates were used in the synthesis of HTlcs by urea method, a large amount of NH_3 and CO_2 produced in the decomposition of urea at high temperature would influence the formation process of the layered double materials. Most of NO_3^-

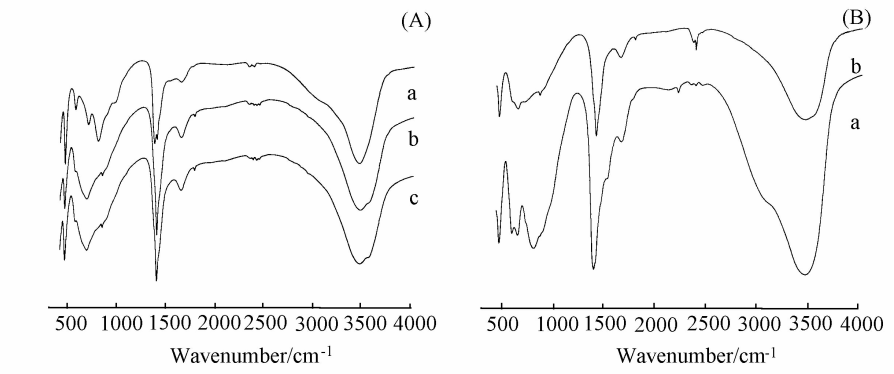
Table 1 Results of elemental analysis for the HTlcs samples

Element	Mg-Al-urea method	Mg-Al-low supersaturation	Mg-Al-high supersaturation	Zn-Al-urea method	Zn-Al-low supersaturation
C	2.37	0.52	0.56	2.02	0.18
H	3.16	3.52	3.52	1.402	1.92
O	28.84	34.49	32.67	21.86	27.03
N	0.45	4.58	4.21	0.20	3.66

reacted with NH_3 and could not enter the interlayer. While CO_3^{2-} entered the interlayer as gallery anions. These were proved by elemental analysis (shown in **Table 1**).

IR analysis is not a diagnostic tool for HTlcs, but it can be useful to identify the presence of the foreign anions in the interlayer between the brucite-like sheets. In addition, the information about the type of bonds formed by the anions and their orientations can also be obtained[1]. It can be seen that the IR spectra of the samples ob-

Figure 2 IR spectra of Mg-Al (A), Zn-Al (B) HTlcs synthesized with different method.



(a) Urea method (urea/NO^{3-}=3, molar ratio); (b) Low super-saturation; (c) High supersaturation

tained by low supersaturation and high supersaturation methods are similar to each other (shown in **Figure 2** (A) curves (b) and (c), (B) curve (b)). But in the case of HTlcs prepared by urea method, the split of the vibration at about 1380 cm^{-1} and a new peak at approximate 790 cm^{-1} appear especially in the spectrum of Mg-Al HTlc (**Figure 2** (A) (a)). These results indicate the difference of the gallery anions in the interlayer between the brucite-like sheets of the HTlcs synthesized with different methods.

In general, the urea method is an advanced pH control method. The crystallinity and the regular degrees in the structure of the products obtained with this method are clearly preferable to those synthesized with other methods.

References

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Received 25 November, 2002