

Synthesis and characterization of colored layered double hydroxides for thermal stabilizer

Liu Xunjun Zhang Yuchao Wang Juan Lei Lixu

(School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China)

Abstract: Colored layered double hydroxides (LDHs) can be synthesized by introducing colored cations such as Fe^{3+} and Cr^{3+} , which can be used as thermal stabilizers for polyvinyl chloride (PVC). The yellowish Mg/Fe and bluish Mg/Cr LDHs are prepared by the co-precipitation method. The results show that the $\text{Mg}_3\text{Cr}_x\text{CO}_3$ and $\text{Mg}_3\text{Fe}_x\text{CO}_3$ colored layered double hydroxides can stabilize PVC for more than 30 min under the thermal aging temperature of 180 °C. The preparation can use cheap $\text{Mg}(\text{OH})_2$ instead of MgCl_2 , which produces a much smaller amount of the by-product NH_4Cl . It is known that NH_4Cl is a cheap fertilizer that is difficult to sell; therefore, the preparation is much greener and more economic than the one using magnesium salt.

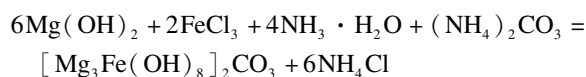
Key words: colored layered double hydroxides; magnesium hydroxide; ferric chloride; chromic chloride; thermal stabilizer; polyvinyl chloride

doi: 10.3969/j.issn.1003-7985.2015.04.023

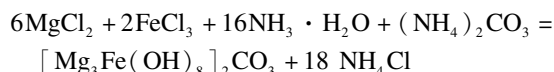
Layered double hydroxides (LDHs) are represented by the general formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}\text{A}^{n-}_{x/n} \cdot y\text{H}_2\text{O}^{[1]}$ (short for $\text{M}_x^{3+}\text{M}_{1-x}^{2+}\text{A}$). In the general formula, M^{2+} and M^{3+} , respectively, stand for divalent and trivalent metal cations, such as Mg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} and so on; A^{n-} stands for intercalated anions, such as Cl^- , NO_3^- and CO_3^{2-} ; n is the charge of the anion; y is the content of interlayer H_2O . Due to the special composition and structure, LDHs have many unique chemical and physical properties, which make them useful as thermal stabilizers^[2-5], fire-retardants^[6-8], absorbents^[9-10], catalysts^[11-12], electrochemically active materials^[13-15] and others^[16-17]. They can be prepared by co-precipitation^[18-19], ion exchange^[20], the hydrothermal method^[21-22], and the calcination regeneration method^[23]. Co-precipitation is one of the most common synthetic methods applied, because the experimental process

can be easily controlled, and the synthetic cycle is relatively shorter.

In the previous studies, the most common precipitating agent was sodium hydroxide; however, a great amount of sodium salt will be produced as a by-product. As we know, sodium salts are cheap and difficult to sell, so we have to decrease the formation of the sodium salt. An attempt has been noted by us, which uses ammonia as the precipitant, and also, $\text{Mg}(\text{OH})_2$ is used instead of MgCl_2 or $\text{Mg}(\text{NO}_3)_2$ as the source of Mg^{2+} ^[24]. By this method, the only by-product, agricultural fertilizer NH_4Cl is formed with only 1/3 amount of previous route, which greatly alleviates the pressure from the by-product. This can be seen from the preparation of $[\text{Mg}_3\text{Fe}(\text{OH})_8]_2\text{CO}_3$ from $\text{Mg}(\text{OH})_2$:



However, if it is prepared from MgCl_2 , the reaction is



It can be seen that three times as much NH_4Cl is formed and four times $\text{NH}_3 \cdot \text{H}_2\text{O}$ is consumed if MgCl_2 is used as a starting material when the same amount of $[\text{Mg}_3\text{Fe}(\text{OH})_8]_2\text{CO}_3$ is formed.

As we know, plastics can be degraded if they are exposed to sunlight for a long time. It is known that the UV light in the sunlight causes the degradation. Transition metals and their compounds such as Fe^{3+} , Cr^{3+} , Zn^{2+} can absorb ultraviolet light well, thus they may protect plastics from ultraviolet radiation. Therefore, it is possible to make multifunctional additives if we introduce transition metals into the LDHs. This paper reports the syntheses of two colored layered double hydroxides, $[\text{Mg}_{1-x}\text{Fe}_x(\text{OH})_2]_2\text{CO}_3$ (short as $\text{Mg}_x\text{Fe}_x\text{CO}_3$) and $[\text{Mg}_{1-x}\text{Cr}_x(\text{OH})_2]_2\text{CO}_3$ (short as $\text{Mg}_y\text{Cr}_x\text{CO}_3$), and their properties.

1 Materials and Experimental Methods

1.1 Chemicals

All the chemicals used were of analytical grade, which were produced by Sinopharm Chemical Reagent Co., Ltd.

Received 2015-01-04.

Biographies: Liu Xunjun (1988—), male, graduate; Lei Lixu (corresponding author), male, doctor, professor, lixu.lei@seu.edu.cn.

Foundation items: The Fundamental Research Funds for the Central Universities, the Scientific Innovation Research of College Graduates in Jiangsu Province (No. CXLX12_0105), the Analysis and Test Fund of Southeast University (No. 201226).

Citation: Liu Xunjun, Zhang Yuchao, Wang Juan, et al. Synthesis and characterization of colored layered double hydroxides for thermal stabilizer[J]. Journal of Southeast University (English Edition), 2015, 31 (4): 566 – 571. [doi: 10.3969/j.issn.1003-7985.2015.04.023]

1.2 Mg/Fe and Mg/Cr layered double hydroxide samples preparation

1.2.1 Preparation of $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$

$\text{Mg}(\text{OH})_2$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were mixed in 150 mL water, which is then added into 100 mL of ammonia water containing ammonium carbonate under stirring. To make Mg_3FeCO_3 with the Mg/Fe molar ratio of 3, the molar ratio of $\text{Mg}(\text{OH})_2$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{CO}_3$ was 3:1:2:0.5. The temperature of the reaction mixture was then raised to make the water reflux, and the pH of the suspension was maintained between 7 and 9, which was continuously stirred for 2 h. After that, the suspension was filtered. Solids were washed with deionized water, and then dried in an oven at 120 °C for 48 h.

$[\text{MgFe}(\text{OH})_8]_2\text{CO}_3$ and $[\text{Mg}_2\text{Fe}(\text{OH})_8]_2\text{CO}_3$ were synthesized similarly with the molar ratio of Mg and Fe being changed according to the chemical formula.

1.2.2 Preparation of $\text{Mg}_y\text{Cr}_z\text{CO}_3$

$\text{Mg}_y\text{Cr}_z\text{CO}_3$ was synthesized by the same method as above, but it was not quite successful. Therefore, MgCl_2 was used instead of $\text{Mg}(\text{OH})_2$; all others were the same except that the amount of ammonia water was increased according to the chemical equation. Therefore, the molar ratio of MgCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{CO}_3$ was 3:1:8:0.5 for the preparation of $[\text{Mg}_3\text{Cr}(\text{OH})_8]_2\text{CO}_3$.

$[\text{MgCr}(\text{OH})_8]_2\text{CO}_3$ and $[\text{Mg}_2\text{Cr}(\text{OH})_8]_2\text{CO}_3$ were also synthesized by changing only the amount of MgCl_2 according to the chemical formula.

1.3 Characterization

Powder X-ray diffraction (XRD) patterns of the samples were performed using a Bruker D8-ADVANCE X-ray diffractometer at 40 kV and 30 mA, with $\text{Cu K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation. Analyses of metals were carried out with a J-A1100 ICP spectrometer. The Fourier transformed infrared spectra (FTIR) of the LDH materials were obtained by using a Nicolet 750 spectrometer. The thermo-gravimetric analysis (TG) of the sample was conducted on a TA Instruments SDT-Q600 in static air with a rate of 10 °C/min.

2 Results and Discussion

2.1 The XRD patterns of the LDHs

Fig. 1 shows the X-ray diffraction patterns of samples prepared under the exploratory conditions (aged for 2 h at the refluxing temperature of water). For $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$, it is observed that the intensities of diffraction peaks increase with the increase of Fe^{3+} content. When the molar ratio of Mg and Fe is 1, the diffraction peaks are almost unobservable (see Fig. 1 (a)). This was observed and believed that more Mg^{2+} could have contributed to the

formation of laminar structure before^[25].

However, it was not very successful when we attempted to synthesize $\text{Mg}_y\text{Cr}_z\text{CO}_3$ in the same method. Fig. 1 (b) shows the result of the attempt. It can be seen that there are the characteristic peaks of the proposed LDHs, but there are still impurity peaks from $\text{Mg}(\text{OH})_2$ which appeared at around 18°^[26]. Thus, the Cr^{3+} cannot react with $\text{Mg}(\text{OH})_2$ as smoothly as Fe^{3+} . Perhaps this is ascribed to the insolubility of $\text{Mg}(\text{OH})_2$ and the inertness in ligand substitution reactions of Cr^{3+} .

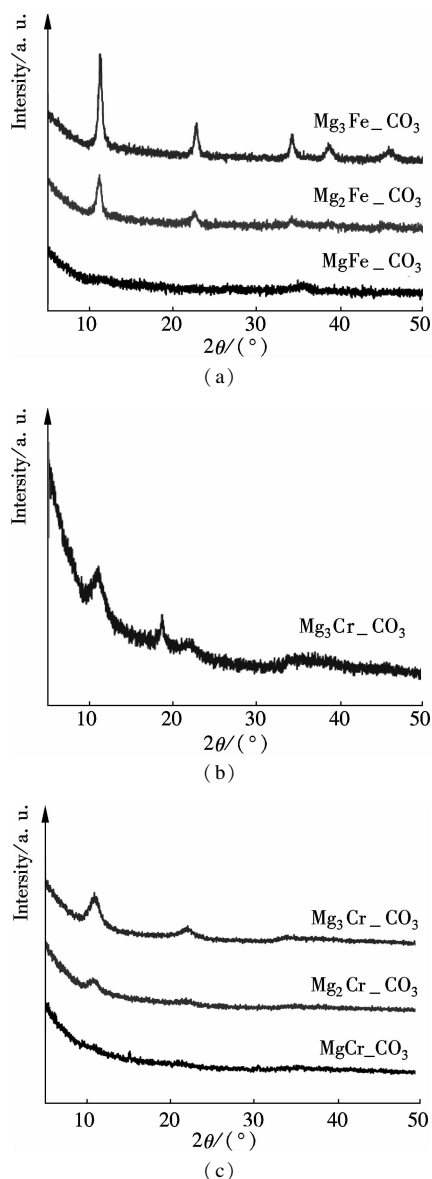


Fig. 1 Powder X-ray diffraction patterns of $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$ products and $\text{Mg}_y\text{Cr}_z\text{CO}_3$ ($y = 1, 2$ and 3). (a) $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$ synthesized from $\text{Mg}(\text{OH})_2$; (b) Mg_3CrCO_3 synthesized from $\text{Mg}(\text{OH})_2$; (c) $\text{Mg}_y\text{Cr}_z\text{CO}_3$ synthesized from MgCl_2

Therefore, we use MgCl_2 instead of $\text{Mg}(\text{OH})_2$ to synthesize $\text{Mg}_y\text{Cr}_z\text{CO}_3$, which is very successful. Fig. 1 (c) shows the related XRD patterns. Similarly, the $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$, $\text{Mg}_y\text{Cr}_z\text{CO}_3$ crystallized better with the increase of the $\text{Mg}^{2+}:\text{Cr}^{3+}$ molar ratio, but they are less well-crystal-

lized than $\text{Mg}_x\text{Fe}_{1-x}\text{CO}_3$. As we have discussed before, this may be also related to the inertness in ligand substitution reactions of Cr^{3+} .

2.2 The IR spectra of as-prepared LDHs

Fig. 2 shows the infrared spectrum of two typical samples. It is clear that both samples display similar characteristics, which is in accordance with the general knowledge on LDHs. The strong and broad band at around $3\,442\text{ cm}^{-1}$ is attributed to the hydroxyl groups stretching mode from both the layer hydroxyl groups and the interlayer water molecules^[27]. The band observed at around $1\,633$ or $1\,639\text{ cm}^{-1}$ is ascribed to the δ_{OH} bending vibration^[28]. The sharp absorption band observed at around $1\,384\text{ cm}^{-1}$ is attributed to the interlayer carbonate^[29–30]. The lattice vibrations of metal-oxygen bonds vibrations likely result from the appearance of the strong bands at 588 cm^{-1} .

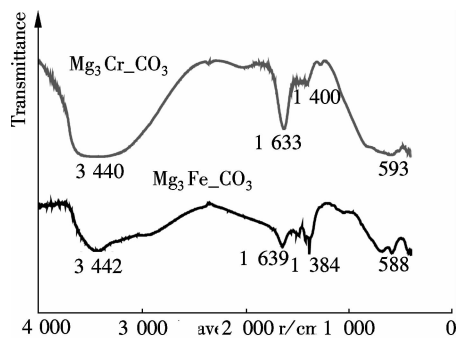


Fig. 2 The FT-IR spectra of $\text{Mg}_3\text{Fe-CO}_3$ and $\text{Mg}_3\text{Cr-CO}_3$ samples

2.3 UV-vis spectrum characterization

The optical absorption behavior of the as-prepared $\text{Mg}_3\text{Fe-CO}_3$ and $\text{Mg}_3\text{Cr-CO}_3$ samples under the exploratory conditions are illustrated by the UV-vis absorption spectrum, as shown in Fig. 3. Both materials show strong UV absorption at around 200 nm, which is assigned to the charge transfer of isolated Fe^{3+} and Cr^{3+} ions octahedrally coordinated in the brucite layered structure^[31]. In the visible light region, the $\text{Mg}_3\text{Fe-CO}_3$ shows absorption at above 400 nm, which is ascribed to the dd transition of Fe^{3+} ^[32]. The $\text{Mg}_3\text{Cr-CO}_3$ exhibits two bands at 419 and 588 nm which can be easily ascribed to spin-allowed, Laporte-forbidden transitions from the fundamental state ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$, respectively, in its brucite layers^[33–34].

2.4 Thermogravimetric studies

Fig. 4 shows the TG-DTA curves of the samples. The $\text{Mg}_3\text{Fe-CO}_3$ roughly undergoes two separate weight loss processes on heating, which is in agreement with studies

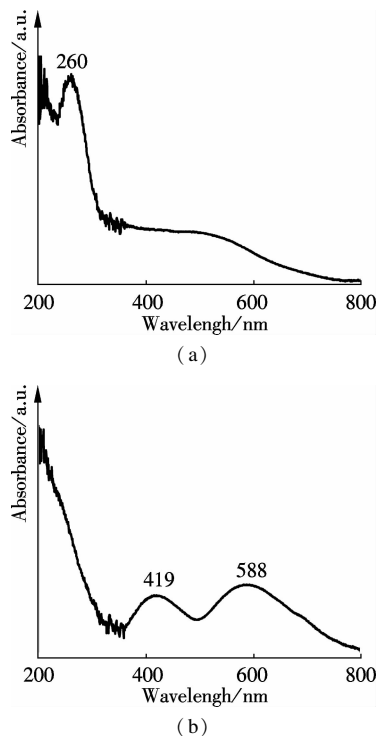


Fig. 3 The UV-vis spectrum. (a) $\text{Mg}_3\text{Fe-CO}_3$ sample; (b) $\text{Mg}_3\text{Cr-CO}_3$ sample

reported on other LDHs^[35]. There are two obvious endothermic peaks at 177.9 and 362.4 °C. The first-step weight loss of 10.8% at about 177.9 °C can result from the loss of interlayer water. The second-step weight loss of 25.9% at about 362.4 °C is due to the dehydroxylation of the layers to form oxides^[36]. If the chemical formula of LDHs is $[\text{Mg}_3\text{Fe}(\text{OH})_8]_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, the loss of the 4 crystal waters will be 10.9% of their weight,

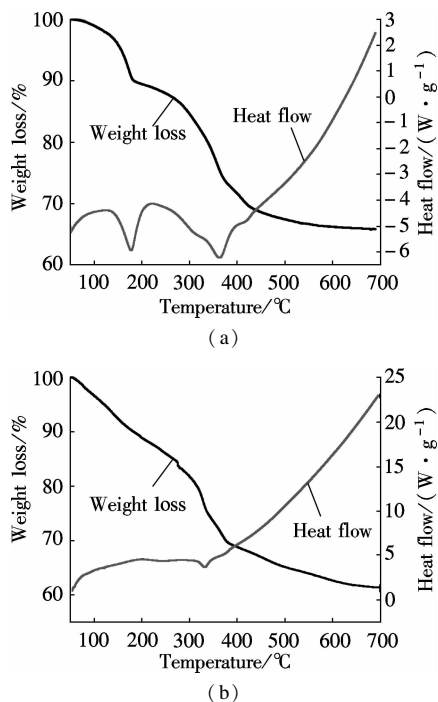


Fig. 4 TG-DTA curves. (a) $\text{Mg}_3\text{Fe-CO}_3$ sample; (b) $\text{Mg}_3\text{Cr-CO}_3$ sample

and the loss of 8 crystal waters from dehydroxylation will be 21.8% of weight. The total loss of weight will be 39.4% , which is very close to the experimental value of 36.7% if the carbonate also decomposes during the thermal decomposition^[37]. The thermal decomposition analysis shows that there is a great loss of the crystal waters which will bring a large amount of heat away and a great deal of loss of water and CO₂ which also brings a large amount of heat away and H₂O and CO₂ will dilute the concentration of O₂ on the surface of be polymer materials. Thus, LDH material can also be used as a flame-retardant.

The TG/DTA behavior of Mg₃Cr_ CO₃ is a slightly different from Mg₃Fe_ CO₃. The weight loss is continuous but the rate is different. The endothermic peaks are not very clear (see Fig.4(b)) , which reveals that there are different ways of decomposition. Perhaps it is related to its initial poor crystallization.

2.5 Thermal stability testing of prepared PVC composites

The PVC composite strips were prepared and made of 100 g PVC powder, 45 g DOP, 0.2 g Zn(st)₂, 0.3 g Ca(st)₂, Mg₃Cr_ CO₃ or Mg₃Fe_ CO₃. The resulting PVC composite strips were placed in a thermal aging test box maintained at 180 °C to observe their color changes. The thermal stability of PVC is defined by the time when the strips become black. As shown in Fig. 5 , the strips

are colored by the LDHs. As the aging time is prolonged , the color of the strips changes. From Fig.5(a) , it can be seen that the color of the blue PVC Mg₃Cr_ CO₃ composite becomes yellow when the time lasts 40 min , then deepens gradually , and finally turns red when the time lasts 90 min. The color of the pale red PVC- Mg₃Cr_ CO₃ composite becomes yellow when the time lasts 50 min , then deepens gradually , and finally turns brown when the time lasts 80 min. It was proposed by Lin et al.^[38] that the stabilization of PVC by LDHs includes two steps. The first step is that HCl produced by the thermal dehydrochlorination of PVC reacts with the interlayer carbonate anions , and then more HCl reacts with the hydroxyl groups in the layers. Those processes remove the HCl which can catalyze the dehydrochlorination of PVC and thus stabilize the PVC material.

3 Conclusion

[Mg₃Fe (OH)₈]₂CO₃ has been successfully prepared from FeCl₃ · 6H₂O , Mg (OH)₂ , NH₃ · H₂O , (NH₄)₂CO₃ in water under refluxing for 2 h. By using Mg(OH)₂ , the amount of by-product NH₄Cl is reduced dramatically. Using Mg(OH)₂ to produce Mg_xCr_ CO₃ is a little difficult , so it is better to use MgCl₂ as the starting material. The existence of Fe³⁺ or Cr³⁺ makes LDHs colored , and they also absorb UV lights. This may make plastics colored and UV-resistant. The decomposition of Mg₃Fe_ CO₃ leads to the weight loss due to the loss of water and CO₂. Similarly , the decomposition of Mg₃Cr_ CO₃ leads to weight loss. This property can allow them to be used as a flame retardant as well as PVC thermal stabilizers. The as-prepared [Mg₃Fe (OH)₈]₂CO₃ and [Mg₃Cr (OH)₈]₂CO₃ were tested as the PVC thermal stabilizers , which show that the former can stabilize PVC for 50 min , and the latter for 30 min at 180 °C.

References

[1] Wang L J , Xu X Y , Evans D G , et al. Synthesis of an N , N-Bis (phosphonomethyl) glycine anion-intercalated layered double hydroxide and its selective infrared absorption effect in low density polyethylene films for use in agriculture[J]. *Ind Eng Chem Res* , 2010 , **49**(11) : 5339 – 5346.

[2] Feng Y J , Tang P G , Xi J M , et al. Layered double hydroxides as flame retardant and thermal stabilizer for polymers[J]. *Recent Patents on Nanotechnology* , 2012 , **6** (3) : 231 – 237.

[3] Ahamad A , Patil C B , Gite V V , et al. Evaluation of the synergistic effect of layered double hydroxides with micro-and nano-Ca₂CO₃ on the thermal stability of polyvinyl chloride composites [J]. *J Thermoplast Compos Mater* , 2013 , **26**(9) : 1249 – 1259.

[4] Yi S , Yang Z H , Wang S W , et al. Effects of MgAlCe- CO₃ layered double hydroxides on the thermal stability of PVC resin[J]. *J Appl Polym Sci* , 2011 , **119**(5) : 2620 –

Fig.5 Thermal stability of composites of polyvinyl chloride. (a) Mg₃Cr_ CO₃ ; (b) Mg₃Fe_ CO₃

2626.

- [5] Wen R J, Yang Z H, Chen H Y, et al. Zn-Al-La hydro-talcite-like compounds as heating stabilizer in PVC resin [J]. *J Rare Earths*, 2012, **30**(9): 895–902.
- [6] Xu S L, Zhang L X, Lin Y J, et al. Layered double hydroxides used as flame retardant for engineering plastic acrylonitrile-butadiene-styrene (ABS) [J]. *J Phys Chem Solids*, 2012, **73**(12): 1514–1517.
- [7] Shi L, Li D Q, Wang J R, et al. Synthesis, flame-retardant and smoke-suppressant properties of a borate-intercalated layered double hydroxide [J]. *Clays Clay Miner*, 2005, **53**(3): 294–300.
- [8] Matusinovic Z, Wilkie C A, Fire retardancy and morphology of layered double hydroxide nanocomposites [J]. *J Mater Chem*, 2012, **22**(36): 18701–18704.
- [9] Guo Y W, Zhu Z L, Qiu Y L, et al. Adsorption of arsenate on Cu/Mg/Fe/La layered double hydroxide from aqueous solutions [J]. *J Hazard Mater*, 2012, **239**: 279–288.
- [10] Mandal S, Mayadevi S. Adsorption of fluoride ions by Zn-Al layered double hydroxides [J]. *Appl Clay Sci*, 2008, **40**(1/2/3/4): 54–62.
- [11] Zhao J K, Xie Y F, Yuan W J, et al. A hierarchical Co-Fe LDH rope-like nanostructure: facile preparation from hexagonal lyotropic liquid crystals and intrinsic oxidase-like catalytic activity [J]. *J Mater Chem B*, 2013, **1**(9): 1263–1269.
- [12] Dubey A. Synthesis and catalytic applications of CMK-LDH (layered double hydroxides) nanocomposite materials [J]. *Green Chem*, 2007, **9**(5): 424–426.
- [13] Zeng L, Zhao T S, Li Y S. Synthesis and characterization of crosslinked poly (vinyl alcohol)/layered double hydroxide composite polymer membranes for alkaline direct ethanol cells [J]. *Int J Hydrog Energy*, 2012, **37**(23): 18425–18432.
- [14] Yarger M S, Steinmiller E M P, Choi K S. Electrochemical synthesis of Zn-Al layered double hydroxide (LDH) films [J]. *Inorg Chem*, 2008, **47**(13): 5859–5865.
- [15] Lei L X, Hu M, Gao X R, et al. The effect of the interlayer anions on the electrochemical performance of layered double hydroxide electrode materials [J]. *Electrochim Acta*, 2008, **54**(2): 671–676.
- [16] Ghotbi M Y, Hussein M Z, Yahaya A H, et al. LDH-intercalated D-gluconate: generation of a new food additive-inorganic nanohybrid compound [J]. *J Phys Chem Solids*, 2009, **70**(6): 948–954.
- [17] Mandel K, Drenkova-Tuhtan A, Hutter F, et al. Layered double hydroxide ion exchangers on superparamagnetic microparticles for recovery of phosphate from waste water [J]. *J Mater Chem A*, 2013, **1**(5): 1840–1848.
- [18] Nyambo C, Songtipya P, Manias E, et al. Effect of MgAl-layered double hydroxide exchanged with linear alkyl carboxylates on fire-retardancy of PMMA and PS [J]. *J Mater Chem*, 2008, **18**(40): 4827–4838.
- [19] Millange F, Walton R I, O'Hare D, Time-resolved in situ X-ray diffraction study of the liquid-phase reconstruction of Mg-Al-carbonate hydrotalcite-like compounds [J]. *J Mater Chem*, 2000, **10**(7): 1713–1720.
- [20] Costantino U, Coletti N, Nocchetti M, et al. Anion exchange of methyl orange into Zn-Al synthetic hydrotalcite and photophysical characterization of the intercalates obtained [J]. *Langmuir*, 1999, **15**(13): 4454–4460.
- [21] Sun G B, Sun L N, Wen H, et al. From layered double hydroxide to spinel nanostructures: Facile synthesis and characterization of nanoplatelets and nanorods [J]. *J Phys Chem B*, 2006, **110**(27): 13375–13380.
- [22] Greenwell H C, Jones W, Rugen-Hankey S L, et al. Efficient synthesis of ordered organo-layered double hydroxides [J]. *Green Chem*, 2010, **12**(4): 688–695.
- [23] Guo Z, Feng J, Feng Y, et al. In situ synthesis of solid base catalysts for the regeneration of degradation products formed during the anthraquinone process for the manufacture of hydrogen peroxide [J]. *Appl Catal A General*, 2011, **401**(1/2): 163–169.
- [24] Zhang L H, Zhu J, Jiang X R, et al. Influence of nature of precursors on the formation and structure of Cu-Ni-Cr mixed oxides from layered double hydroxides [J]. *J Phys Chem Solids*, 2006, **67**(8): 1678–1686.
- [25] Vulic T, Reitzmann A, Ranogajec J, et al. The influence of synthesis method and Mg-Al-Fe content on the thermal stability of layered double hydroxides [J]. *J Therm Anal Calorim*, 2012, **110**(1): 227–233.
- [26] Sierra-Fernandez A, Gomez-Villalba L S, Milosevic O, et al. Synthesis and morpho-structural characterization of nanostructured magnesium hydroxide obtained by a hydrothermal method [J]. *Ceramics International*, 2014, **40**(8): 12285–12292.
- [27] Kagunga W, Baddour-Hadjean R, Kooli F, et al. Vibrational modes in layered double hydroxides and their calcined derivatives [J]. *Chem Phys*, 1998, **236**(1/2/3): 225–234.
- [28] Constantino V R L, Pinnavaia T J. Basic properties of $Mg^{2+}_xAl^{3+}_x$ layered double hydroxides intercalated by carbonate, hydroxide chloride and sulfate anions [J]. *Inorg Chem* 1995, **34**(4): 883–892.
- [29] Du L C, Qu B L. Structural characterization and thermal oxidation properties of LLDPE/MgAl-LDH nanocomposites [J]. *J Mater Chem*, 2006, **16**(16): 1549–1554.
- [30] O'Leary S, O'Hare D, Seeley G. Delamination of layered double hydroxides in polar monomers: new LDH-acrylate nanocomposites [J]. *Chem Commun* 2002, (14): 1506–1507.
- [31] Heredia A I C, Oliva M I, Zandalazini C I, et al. Synthesis, characterization, and catalytic behavior of Mg-Al-Zn-Fe mixed oxides from precursors layered double hydroxide [J]. *Ind Eng Chem Res*, 2011, **50**(11): 6695–6703.
- [32] Parida K, Satpathy M, Mohapatra L. Incorporation of Fe^{3+} into Mg/Al layered double hydroxide framework: effects on textural properties and photocatalytic activity for H_2 generation [J]. *J Mater Chem*, 2012, **22**(15): 7350–7357.
- [33] Liu J W, Chen G, Li Z H, et al. Electronic structure and visible light photocatalysis water splitting property of chromium-doped $SrTiO_3$ [J]. *J Solid State Chem*, 2006, **179**(12): 3704–3708.
- [34] Guo Y, Zhang H, Zhao L, et al. Synthesis and characterization of Cd-Cr and Zn-Cd-Cr layered double hydroxides intercalated with dodecyl sulfate [J]. *J Solid State Chem*, 2005, **178**(6): 1830–1836.

[35] Spratt H J, Palmer S J, Frost R L, Thermal decomposition of synthesised layered double hydroxides based upon Mg/(Fe,Cr) and carbonate[J]. *Thermochimica Acta*, 2008, **479**(1/2): 1-6.

[36] Wang Y L, Wu P X, Li B, et al. In-depth study on intercalating threonine into layered double hydroxides[J]. *Appl Clay Sci*, 2011, **53**(4): 615-620.

[37] Moscovitz H, Lando D, Cohen H, et al. Bishophite chlorination[J]. *Ind Eng Chem Prod Res Dev*, 1978, **17**(2): 156-160.

[38] Lin Y J, Li D Q, Evans D G, et al. Modulating effect of Mg-Al-CO₃ layered double hydroxides on the thermal stability of PVC resin[J]. *Polym Degrad Stab*, 2005, **88**(2): 286-293.

用作热稳定剂的有色层状氢氧化物的合成与表征

刘循军 张玉超 王娟 雷立旭

(东南大学化学化工学院,南京 211189)

摘要:通过引入 Fe³⁺、Cr³⁺ 等有色金属阳离子可以得到有色层状氢氧化物,该有色层状氢氧化物可用作聚氯乙烯热稳定剂. 通过共沉淀法分别制备了浅黄色的 Mg/Fe 层状氢氧化物和浅蓝色的 Mg/Cr 层状氢氧化物. 研究表明,在 180 ℃热老化温度下,Mg₃Cr-CO₃ 和 Mg₃Fe-CO₃ 层状氢氧化物可使聚氯乙烯塑料保持稳定超过30 min. 研究发现实验采用氢氧化镁代替可溶性的镁盐,例如六水合氯化镁等,可以大幅减少副产物氯化物的生成. 由于氯化铵是一种廉价的化肥且难以处理,因此,与采用镁盐的制备方法相比,所提的制备方法更为绿色经济环保.

关键词:有色层状氢氧化物;氢氧化镁;氯化铁;氯化铬;热稳定剂;聚氯乙烯

中图分类号:TQ047