Journal of Materials Science & Surface Engineering Vol. 4 (7), 2016, pp 488-491

Contents lists available at http://www.jmsse.org/

Journal of Materials Science & Surface Engineering

Synthesis and Characterization of Layered Double Hydroxides with divalent ions (Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+})

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Article history

Received: 23-Oct-2016
Revised: 17-Nov-2016
Available online: 02-Dec-2016

Keywords:
Layered Double Hydroxides,
Divalent ions,
A hydrothermal method,
Hydrolysis of urea.

Abstract

Layered double hydroxides (LDHs) with different divalent ions (Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}) were successfully synthesized by a hydrothermal method induced by slow hydrolysis of urea. The as-synthesized samples were characterized by X-ray diffraction (XRD) analysis, thermogravimetric (TG) analysis, and scanning electron microscopy (SEM). From the SEM results, we can concede that the morphology of LDHs is dependent on the divalent ions. LDHs Mg/Al and LDH Co/Al sample exhibit hexagonal platelet morphology with the micro scale . Differently, in LDH Ni/Al sample, the SEM image shows that these LDHs exhibit 3D microflower structure constructed by plentiful intercalated round nanoplates, while the irregular shape and size was observed in three remain samples (LDHs Cu/Al, LDHs Ca/Al, and LDHs Zn/Al sample).

Introduction

Layered double hydroxides (LDHs), hydrotalcite-like compounds or anionic clays, have received considerable attention due to their unique layer structure and anion exchange capability. LDHs foundwidespread applications in areas such as [1–3], adsorbents [4,5], anion exchangers [6–8], and in biochemistry [9–11].
It is well-known fact that the LDHs structure consists of brucite layers where a partial M^{2+}/M^{3+} substitution has taken place, thus requiring interlayer anions to balance the positive charge of the layers. The general formula is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}.mH_2O]$, where $x = M^{3+}/(M^{2+}+M^{3+})$ and n is the formal charge of the anion. M^{2+} can be Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}. M^{3+} can be Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, and Mn^{3+}. The interlayer anion A can be Cl^-, NO^{3-}, CO_3^{2-}, or organic anions.

It is documented that the synthesis methods can significantly affect the morphology, size, surface area and phase structure of LDHs. The main synthesis approaches of LDHs include coprecipitation [12], reconstruction [13], anion exchange[14], glycerol-effected exchange[15], and homogeneous precipitation[16]. Hydrothermal synthesis method has also been employed produce LDHs because they have a distinct effect on the crystalline morphology and crystalline phase.

In this study, we report on a one-step hydrothermal approach induced by slow hydrolysis of urea for synthesizing LDHs with different divalent ions (Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}). Full characterization of the solids prepared has been achieved using X-ray diffraction (XRD) analysis, FT-IR, thermogravimetric (TG) analysis, and scanning electron microscopy (SEM).

Experimental

$Mg(NO_3)_2.6H_2O$ (≥99.9%), $Al(NO_3)_3.9H_2O$ (≥98.0%), $Cu(NO_3)_2.3H_2O$ (≥94.0%), $Ca(NO_3)_2.4H_2O$ (≥99.0%), $Ni(NO_3)_2.6H_2O$ (≥98.5%), $Co(NO_3)_2.6H_2O$ (≥98.0%), $Zn(NO_3)_2.6H_2O$ (≥98.0%), and urea were purchased from Aldrich and used as received. LDHs were synthesized by homogeneous precipitation method using urea hydrolysis method [30]. For the synthesis of Mg/Al LDH, a mixture of $Mg(NO_3)_2.6H_2O$ (6.7 mmol), $Al(NO_3)_3.9H_2O$ (3.3 mmol), and urea (20 mmol) was dissolved in 100 mL distilled water with magnetic stirring at room temperature. The resulting clear solution was transferred into a Teflon-lined autoclave and heated at 150 °C for 24h. The solid precipitate was separated by centrifugation and washed with distilled water subsequently. The final product (LDH Mg/Al) was dried at 90 °C till constant weight. LDHs containing cobalt or nickel were prepared with the same methods as the preparation of LDH Mg/Al sample by the replacing $Mg(NO_3)_2.6H_2O$ with $Cu(NO_3)_2.6H_2O$, $Ca(NO_3)_2.6H_2O$ $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ or $Zn(NO_3)_2.6H_2O$. The obtained samples were named as LDH Cu/Al, LDH Ca/Al, LDH Ni/Al, LDH Co/Al and LDH Zn/Al, respectively.

Thermogravimetric analysis (TGA) carried out at a heating rate of 10°/min under an air flux up to 900 °C using a Perkin-Elmer Pyris 1 analyzer. The crystal structures of LDHs samples were examined by powder X-ray diffraction (XRD) patterns with Cu Kα radiation (λ = 1.5405 Å) in the 2θ range of 5-80° (Philips X'pert-MPD, Netherlands). The changes in the surface chemical were investigated by Fourier Transformed Infrared Spectrophotometry (FT-IR) using a BOMEM Hartman & Braun FT-IR Spectrometer in the frequency range of 4000 - 400 cm^{-1}. The morphology of the samples was investigated by Field Emission Scanning Electron Microscopy (FE-SEM) using a JSM-6700F (Japan) at an accelerating voltage of 120 kV.

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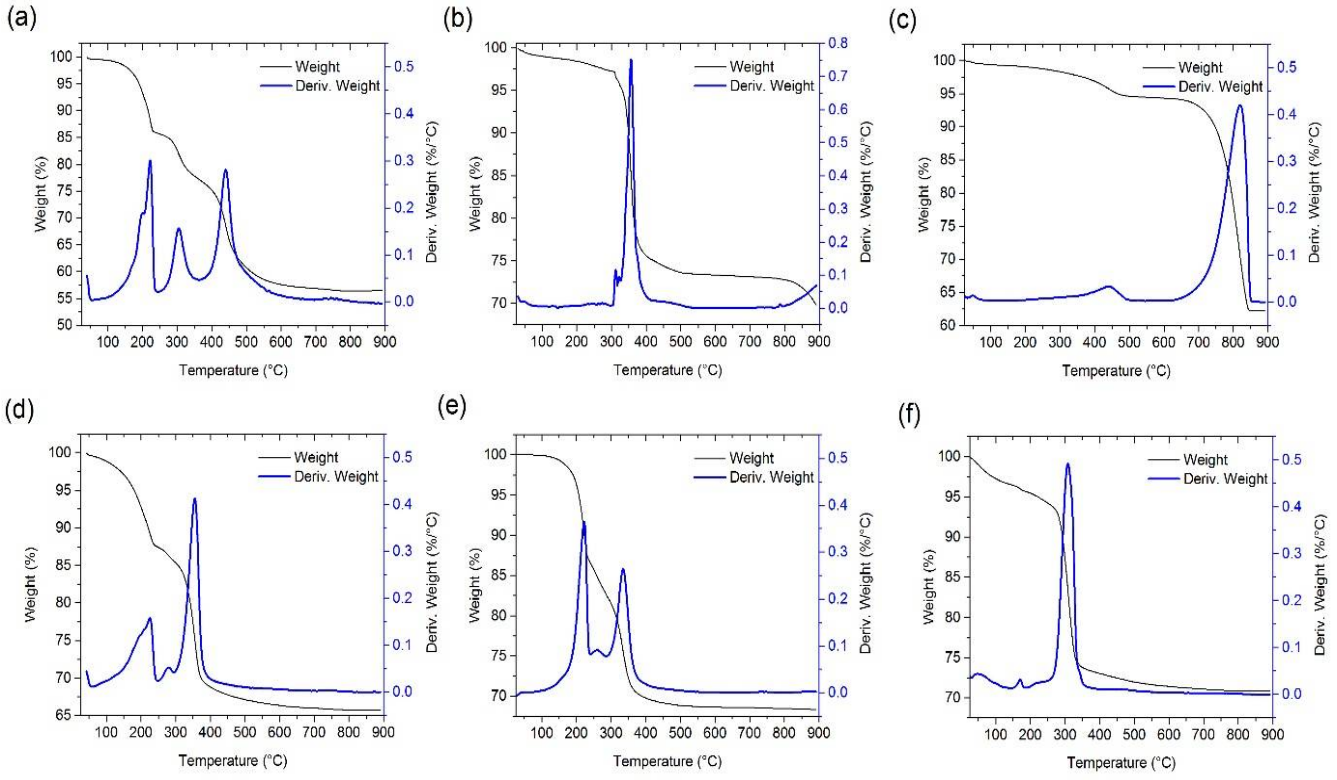

Figure 1: The TG/DTA of LDHs samples: (a) LDH Mg/Al, (b) LDH Cu/Al, (c) LDH Ca/Al, (d) LDH Ni/Al, (e) LDH Co/Al, and (f) LDH Zn/Al

Results and Discussion

Layered double hydroxides (LDHs) with different divalent ions (Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}) were successfully synthesized by a one-step hydrothermal method induced by slow hydrolysis of urea. TGA analysis was used to analyze the thermal evolution of the LDHs samples, as shown in Fig. 1. Generally, all sample displays two degradation patterns: (i) An initial weight loss corresponds to the evaporation of water including adsorbed water and dehydration of interlamellar water; (ii) a second mass loss ascribes to the dehydroxylation of the lattices and decomposition of the interlayer anions, resulting in a final product that is a mixture of magnesium (copper; Ca; Ni; Co; or Zn) aluminium oxides [17,18]. However, in the Mg/Al LDH the TGA data shows less-defined decomposition ranges, indicative of the phase impurity malachite.

The crystalline structure of the as-prepared LDHs samples was determined by XRD. The XRD patterns of the LDHs Mg/Al samples, shown in Fig. 2a, exhibit the rhombohedral structure of LDHs Mg/Al (JCPDS card no. 22-700) [19]. The XRD patterns consist of peaks at 2θ values of 11.7, 23.6, 60.1, 62°, corresponding to the sharp and symmetric reflections for (003), (006), (110) and (113) planes, respectively; the XRD patterns consist of peaks at 2θ values of 35, 39.6, 47°, corresponding to the broad and asymmetric reflections for (012), (015), and (018) planes, respectively [20,21]. No crystalline phase containing oxide peaks were detected in the LDH Mg/Al sample. Fig. 2b displays the XRD patterns of LDHs Cu/Al sample. All of the diffraction peaks can be ascribed to copper aluminium carbonate hydroxide hydrate (JCPDS card no.37-630) and no impurity peak can be observed, indicating that the procedure employed in this study produces an LDH crystal with a well-defined structure [22]. Fig. 2c shows the XRD patterns of LDHs Ca/Mg. As shown in Fig. 2c, there are no peaks indexing the characteristic reflections of layered double hydroxides, indicating that an LDH crystal with a well-defined structure was not produced in this our condition reaction. Fig. 2d depicts the XRD patterns of the LDHs Ni/Al samples with all peaks indexing the characteristic reflections of layered double hydroxides (JCPDS card no. 15-0087) [23].

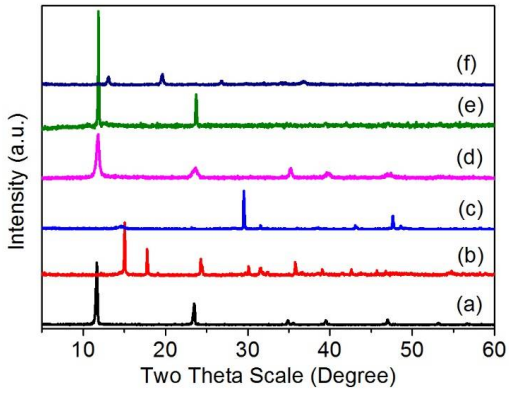

Figure 2: The XRD patterns of LDHs samples: (a) LDH Mg/Al, (b) LDH Cu/Al, (c) LDH Ca/Al, (d) LDH Ni/Al, (e) LDH Co/Al, and (f) LDH Zn/Al

Characteristic sharp diffraction peaks were indexed as (003), (006), and (009) and broad asymmetric peaks were indexed as (015) and (018). Similarly, The XRD patterns of the LDHs Co/Al samples, shown in Fig. 2e, exhibit the rhombohedral structure of LDHs Co/Al (JCPDS card no. 51-0045) with the characteristic peaks of (003) and (006) planes [24]. The XRD patterns of the

LDHs Zn/Al samples was shown in Fig. 2f. The result indicated that an LDH crystal with a well-defined structure was not produced in this our condition reaction because there are no peaks indexing the characteristic reflections of layered double hydroxides.

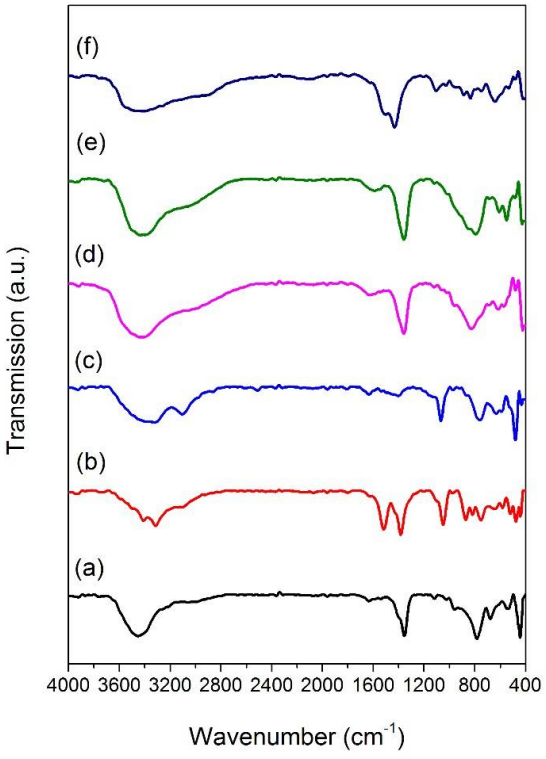

Figure 3: The FTIR of LDHs samples: (a) LDH Mg/Al, (b) LDH Cu/Al, (c) LDH Ca/Al, (d) LDH Ni/Al, (e) LDH Co/Al, and (f) LDH Zn/Al

The presence of surfactant in the interlayer region is confirmed from the FT-IR spectra of LDHs samples (Fig.3). In all the spectrum of LDHs, the broad band peak at around 3500 cm^{-1} can be ascribed to the stretching vibration of Al-OH/H_2O on the LDHs. The bands which appear from 1000 to 500 cm^{-1} can be attributed to the interlayer CO_3^{2-}. The lattice vibration bands at 400–800 cm^{-1} are associated to M–O and O–M–O groups.

The surface morphologies of the as-prepared LDHs samples could be visualized by using SEM characterization as shown in Fig. 4. From the SEM images, the morphologies and shapes of LDHs samples varied according to the divalent ions (M^{II}) such as Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}. This result was conceded that the morphology of LDHs is dependent on the divalent ions. For example, LDHs Mg/Al and LDH Co/Al sample exhibit hexagonal platelet morphology with the micro scale (Fig. 4a and Fig. 4e, respectively). Differently, in LDH Ni/Al sample, the SEM image shows that these LDHs exhibit 3D microflower structure constructed by plentiful intercalated round nanoplates. In addition, the irregular shape and size were observed in three remain samples (LDHs Cu/Al, LDHs Ca/Al, and LDHs Zn/Al sample).

Conclusions

Highly crystallized Layered double hydroxides (LDHs) with different divalent ions (Mg^{2+}, Cu^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}) were successfully synthesized by a hydrothermal method induced by slow hydrolysis of urea. The physical properties of the synthesized LDHs were investigated by XRD, FE-SEM, FT-IR, and TGA. The results show that the morphology of LDHs is dependent on the divalent ions. LDHs Mg/Al and LDH Co/Al sample exhibit hexagonal platelet morphology with the micro scale . Differently, in LDH Ni/Al sample, the SEM image shows that these LDHs exhibit 3D microflower structure constructed by plentiful intercalated round nanoplates, while the irregular shape and size was observed in three remain samples (LDHs Cu/Al, LDHs Ca/Al, and LDHs Zn/Al sample).

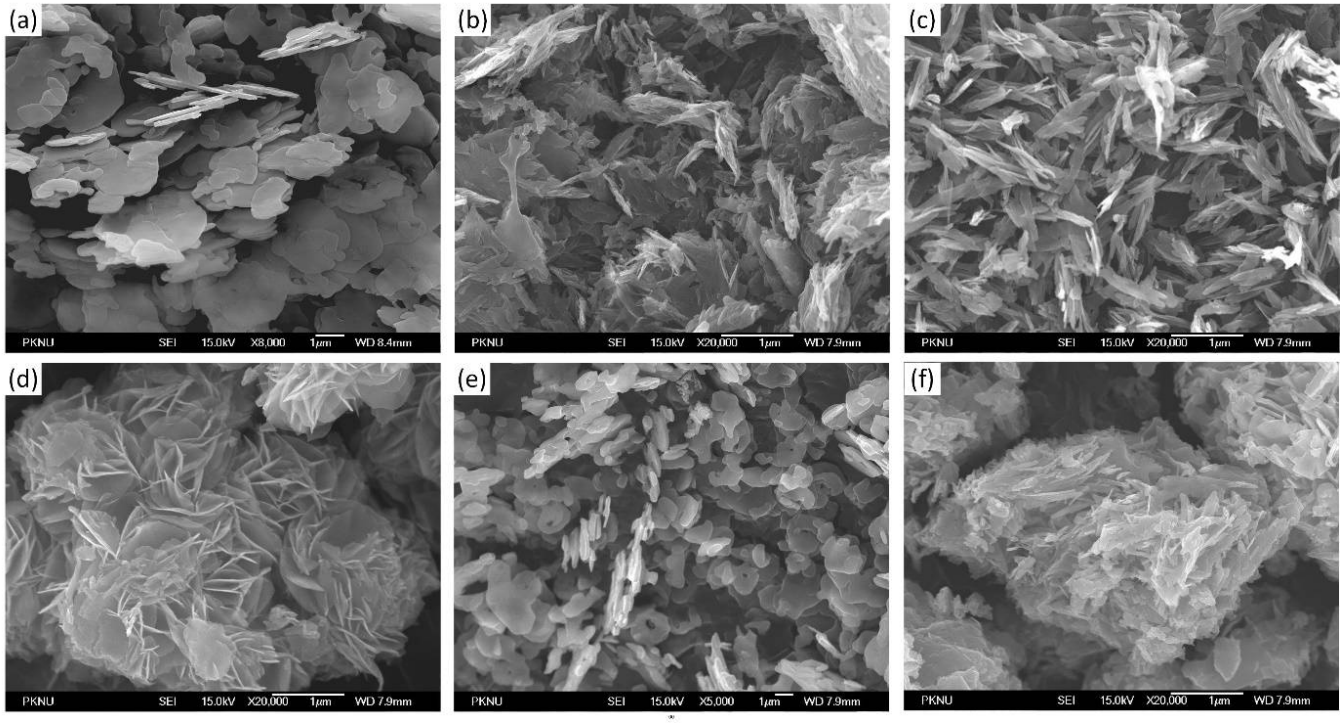

Figure 4: SEM images of LDHs samples: (a) LDH Mg/Al, (b) LDH Cu/Al, (c) LDH Ca/Al, (d) LDH Ni/Al, (e) LDH Co/Al, and (f) LDH Zn/Al.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.02-2014.53.

References

1. Z.P. Xu, J. Zhang, M.O. Adebajo, H. Zhang, C. Zhou, Appl. Clay Sci. 53 (2011) 139–150.
2. F. Zhang, X. Xiang, F. Li, X. Duan, Catal. Surv. from Asia 12 (2008) 253–265.
3. F. Song, X. Hu, Nat. Commun. 5 (2014) 1–9.
4. Q. Wang, H.H. Tay, Z. Zhong, J. Luo, A. Borgna, Energy Environ. Sci. 5 (2012) 7526.
5. I. Dékány, F. Berger, K. Imrik, G. Lagaly, Colloid Polym. Sci. 275 (1997) 681–688.
6. M. Meyn, K. Beneke, G. Lagaly, Inorg. Chem (1990) 5201–5207.
7. D.E. De Vos, J. Wahlen, B.F. Sels, P.A. Jacobs, Synlett (2002) UNSP 1437–2096,E;2002,0,03,0367,0380,ftx,en;A28001.
8. S.J. Palmer, R.L. Frost, T. Nguyen, Coord. Chem. Rev. 253 (2009) 250–267.
9. J.H. Choy, S.J. Choi, J.M. Oh, T. Park, Appl. Clay Sci. 36 (2007) 122–132.
10. C. Del Hoyo, Appl. Clay Sci. 36 (2007) 103–121.
11. V. Rives, M. del Arco, C. Martín, Appl. Clay Sci. 88-89 (2014) 239–269.
12. S. Miyata, Clays Clay Miner. 28 (1980) 50–56.
13. B.R. Venugopal, C. Shivakumara, M. Rajamathi, Solid State Sci. 9 (2007) 287–294.
14. A. V. Radha, P.V. Kamath, C. Shivakumara, Solid State Sci. 7 (2005) 1180–1187.
15. S. Wiesen, N. Tippkötter, K. Muffler, K. Suck, U. Sohling, F. Ruf, R. Ulber, Adsorption 21 (2015) 459–466.
16. N. Iyi, K. Tamura, H. Yamada, J. Colloid Interface Sci. 340 (2009) 67–73.
17. J.H. Choy, J.S. Jung, J.M. Oh, M. Park, J. Jeong, Y.K. Kang, O.J. Han, Biomaterials 25 (2004) 3059–3064.
18. M. Ardanuy, J.I. Velasco, Appl. Clay Sci. 51 (2011) 341–347.
19. T. Kameda, M. Saito, Y. Umetsu, Mater. Trans. 47 (2006) 923–930.
20. J. Han, X. Xu, X. Rao, M. Wei, D.G. Evans, X. Duan, J. Mater. Chem. 21 (2011) 2126.
21. Z. Wang, F. Liu, C. Lu, Chem. Commun. (Camb). 47 (2011) 5479–81.
22. Y. Lwin, M.A. Yarmo, Z. Yaakob, A.B. Mohamad, W.R.W. Daud, Mater. Res. Bull. 36 (2001) 193–198.
23. R. Wang, Q. Li, N. Duan, T. Zhang, H. Lu, Res. Chem. Intermed. 41 (2015) 7899–7914.
24. T. Xu, X. Wu, Y. Li, W. Xu, Z. Lu, Y. Li, X. Lei, X. Sun, ChemElectroChem 2 (2015) 679–683.

