

## Influence of nature of the precipitating agent and chemical-thermal treatment on the phase composition of cerium-containing layered double hydroxides

© Sergey N. Golovin, Maksim N. Yaprincev, Irina G. Ryltsova, and Olga E. Lebedeva\*<sup>†</sup>

General Chemistry Department. Institute of Pharmacy. Chemistry and Biology.

Belgorod National State Research University. Pobedy St., 85. Belgorod, 308015. Russia.

Phone: +7 (422) 30-11-66. E-mail: OLebedeva@bsu.edu.ru

\*Supervising author; <sup>†</sup>Corresponding author

**Keywords:** layered double hydroxides, hydrothermal synthesis, cerium, coprecipitation.

### Abstract

The synthesis of rare earth containing layered double hydroxides is connected with several problems, because the ionic radii of rare earth metal cations are quite large. In the case of cerium, its trivalent cation is easily oxidized to tetravalent state, and this adds more difficulties. In the current paper, coprecipitation method followed by hydrothermal or microwave-hydrothermal treatment was selected for obtaining nickel-cerium-aluminum layered double hydroxide. Urea or sodium hydroxide was used as precipitating agent. Aluminum, nickel and cerium nitrates taken in stoichiometric ratio served as precursors for the syntheses. Powder X-ray diffraction shows reflections of impurity phase, which belong to tetravalent cerium compounds (presumably it was cerium(IV) oxide) in all samples obtained with urea hydrolysis. Using sodium hydroxide under microwave-hydrothermal conditions does not allow reaching the desired result. Oxidation of cerium(III) to cerium(IV) is likely to occur faster than the precipitation and formation of layered structure. Creation of reducing media by means of ethylene glycol addition did not prevent the oxidation though it decreased a content of cerium oxide in products. The most efficient technique for incorporation cerium into the structure of metal-hydroxide layers is coprecipitation with sodium hydroxide followed by hydrothermal treatment. This method allows obtaining single phase cerium-containing layered double hydroxide with good crystallinity. Incorporation of cerium is confirmed by energy-dispersive X-ray spectroscopy. Cerium content was shown to achieve 3%.

### References

- [1] M. Sarfraz, I. Shakir. Recent advances in layered double hydroxides as electrode materials for high-performance electrochemical energy storage devices. *J. Energ. Storage*. **2017**. Vol.13 P.103-122.
- [2] G. Abellán, C. Martí-Gastaldo, A. Ribera, E. Coronado. Hybrid Materials Based on Magnetic Layered Double Hydroxides: A Molecular Perspective. *Acc. Chem. Res.* **2015**. Vol.48. No.6. P.1601-1611.
- [3] N. Ahmed, Y. Shibata, T. Taniguchi, Y. Izumi. Photocatalytic conversion of carbon dioxide into methanol using zinc-copper-M(III) (M = aluminum, gallium) layered double hydroxides. *J. Catal.* **2011**. Vol.279. No.1. P.123-135.
- [4] A. Mantilla, F. Tzompantzi, J.L. Fernández, J.A.I. Díaz Góngora, G. Mendoza, R. Gómez. Photodegradation of 2,4-dichlorophenoxyacetic acid using ZnAlFe layered double hydroxides as photocatalysts. *Catal. Today*. **2009**. Vol.148. No.1. P.119-123.
- [5] A.B. Béléké, M. Mizuhata. Electrochemical properties of nickel-aluminum layered double hydroxide/carbon composite fabricated by liquid phase deposition. *J. Power Sources*. **2010**. Vol.195. No.22. P.7669-7676.
- [6] X.-M. Liu, Y.-H. Zhang, X.-G. Zhang, S.-Y. Fu. Studies on Me/Al-layered double hydroxides (M = Ni and Co) as electrode materials for electrochemical capacitors. *Electrochim. Acta*. **2004**. Vol.49. No.19. P.3137-3141.
- [7] J. Pérez-Ramírez, A. Ribera, F. Kapteijn, E. Coronado, C.J. Gómez-García. Magnetic properties of Co-Al, Ni-Al, and Mg-Al hydrotalcites and the oxides formed upon their thermal decomposition. *J. Mater. Chem.* **2002**. Vol.12. P.2370-2375.
- [8] H. Yan, J. Wang, Y. Zhang, W. Hu. Preparation and inhibition properties of molybdate intercalated ZnAlCe layered double hydroxide. *J. Alloys Compd.* **2016**. Vol.678. P.171-178.

- [9] Y. Zhang, J. Liu, Y. Li, M. Yu, X. Yin, S. Li. Enhancement of Active Anticorrosion via Ce-doped Zn-Al Layered Double Hydroxides Embedded in Sol-Gel Coating on Aluminum Alloy. *J. Wuhan Univ. Technol.-Mat. Sci. Edit.* **2017**. Vol.32. No.5. P.1199-1204.
- [10] X. Wang, Y. Chen, H. Zhou, K. Zhang. Structure and photoluminescence of a new binary Mg/Tb layered double hydroxide. *Appl. Clay Sci.* **2017**. Vol.150. P.184-191.
- [11] J. He, M. Wei, B. Li, Y. Kang, D.G. Evans, X. Duan. Layered Double Hydroxides. *In: Structure and Bonding*. Vol.119. P.89-119.
- [12] S. Miyata. The Syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties I: The systems  $Mg^{2+}-Al^{3+}-NO_3^-$ ,  $Mg^{2+}-Al^{3+}-Cl^-$ ,  $Mg^{2+}-Al^{3+}-ClO_4^-$ ,  $Ni^{2+}-Al^{3+}-Cl^-$  and  $Zn^{2+}-Al^{3+}-Cl^-$ . *Clays Clay Miner.* **1975**. Vol.23. No.5. P.369-375.
- [13] Y. Han, Z.-H. Liu, Z. Yang, Z. Wang, X. Tang, T. Wang, L. Fan, K. Ooi. Preparation of  $Ni^{2+}-Fe^{3+}$  Layered Double Hydroxide Material with High Crystallinity and Well-Defined Hexagonal Shapes. *Chem. Mater.* **2008**. Vol.20. No.2. P.360-363.
- [14] M. Joy, S.J. Iyengar, J. Chakraborty, S. Ghosh. Layered double hydroxide using hydrothermal treatment: morphology evolution, intercalation and release kinetics of diclofenac sodium. *Front. Mater. Sci.* **2017**. Vol.11. No.4. P.395-408.
- [15] G. Mishra, B. Dash, S. Pandey. Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials. *Appl. Clay Sci.* **2018**. Vol.153. P.172-186.
- [16] U. Constantino, F. Marmottini, M. Nocchetti, R. Vivani. New Synthetic Routes to Hydrotalcite-Like Compounds – Characterization and Properties of the Obtained Materials. *Eur. J. Inorg. Chem.* **1998**. Vol.1998. No.10. P.1439-1446.
- [17] M. Suárez-Quezada, G. Romero-Ortiz, V. Suárez, G. Morales-Mendoza, L. Lartundo-Rojas, E. Navarro-Cerón, F. Tzompantzi, S. Robles, R. Gómez, A. Mantilla. Photodegradation of phenol using reconstructed Ce doped Zn/Al layered double hydroxides as photocatalysts. *Catal. Today.* **2016**. Vol.271. P.213.
- [18] M. Adachi-Pagano, C. Forano, J.-P. Besse. Synthesis of Al-rich hydrotalcite-like compounds by using the urea hydrolysis reaction – control of size and morphology. *J. Mater. Chem.* **2003**. Vol.13. No.8. P.1988-1993.