



SYNTHESIS OF Ni(II)-Ti(IV) LAYERED DOUBLE HYDROXIDES USING COPRECIPITATION AT HIGH SUPERSATURATION METHOD

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ABSTRACT

The aim of the work was to prepare Ni(II)-Ti(IV) layered double hydroxides using co precipitation at high super saturation method, which has not been reported yet. The samples were prepared using co precipitation at high super saturation, by adding mixed salt ($\text{Ni}^{2+} + \text{Ti}^{4+}$) solution to $\text{NaOH} + \text{Na}_2\text{CO}_3$ solution. The prepared samples were characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TG) and Differential Scanning Calorimetry. The results of XRD analysis has confirmed that prepared samples have hydrotalcite-like structure, isomorphous to $\alpha\text{-Ni}(\text{OH})_2$. Separate titanium oxide or hydroxide phase was not observed. The influence of synthesis temperature and hydrothermal treatment on phase composition, morphology, and thermal stability has been studied using TG, DSC, and SEM. It has been established that elevated synthesis temperature and hydrothermal affect crystallinity, thermal stability and morphology, but no effect on phase composition was observed. A formation mechanism of Ni (II)-Ti (IV) layered double hydroxide during co precipitation at high super saturation have been proposed.

Keywords: layered double hydroxide, co precipitation, nickel, titanium.

1. INTRODUCTION

Layered double hydroxides (LDH) or hydrotalcite-like compounds - are a class of synthetic and natural compounds with general formula $[\text{M}_1^{2+}\text{M}_2^{3+}(\text{OH})_2]^{x+}[\text{A}_{x/m}]^{m-}\cdot n\text{H}_2\text{O}$, where: M^{2+} - a divalent cation (Ni^{2+} , Mg^{2+} , Zn^{2+} , Ca^{2+} , Fe^{2+} etc.); M^{3+} - trivalent cation (Al^{3+} , Fe^{3+} , Cr^{3+} etc.); A - anion (CO_3^{2-} , Cl^- , OH^- , $[\text{Fe}(\text{CN})_6]^{3-/4-}$ etc.). They have layered structure similar to brucite ($\text{Mg}(\text{OH})_2$), but with partial substitution of a divalent cation by trivalent ones. Such substitution generates an additional positive charge which is compensated by anions, residing in between layers with water [1].

Literature analysis revealed that layered double hydroxide is usually prepared from the solution containing di- and trivalent metal salts using various coprecipitation methods [2]. Other methods for synthesis of hydroxides such as electrolysis [3-5], template [6] and high-temperature synthesis [7] can also be used. Common synthesis methods for preparation of layered doubled hydroxides are:

Titration method. A drop-wise addition of the basic solution (NaOH , KOH) into the solution containing the mixture of metal salts (M^{2+} and M^{3+}).

Coprecipitation at high supersaturation. A drop-wise addition of a solution containing mixed metal salts (M^{2+} and M^{3+}) into alkaline solution (NaOH , KOH).

Homogeneous coprecipitation. During homogeneous coprecipitation, a mixed salt solution is (M^{2+} and M^{3+}) mixed with ammonia releasing agent

(usually urea). The solution is then heated, to a hydrolysis temperature of ammonia realizing agent. Hydrolysis leads to a slow release of ammonia into solution, causing a pH increase which leads to coprecipitation. Presence of ammonia in a solution can complicate LDH formation due to the formation of soluble ammine complexes.

According to literature the tetravalent cations, such as Ti^{4+} also capable of LDH structure formation [8-15]. They play the same role as trivalent cations but create excessive charge $2x$.

Ni-Ti LDH can be characterized as titanium stabilized $\alpha\text{-Ni}(\text{OH})_2$, thus having the same range of application as nickel hydroxide: battery electrode material [16-21], electrochromic films [22-25], electro oxidation catalyst [26]. Presence of structural titanium allows for application as anion-exchange and anion-absorption material [10], anion-support [11, 27], photocatalyst [13-14] etc.

Homogeneous coprecipitation is the most common methods for Ni-Ti LDH preparation [9-12]. However, such a synthesis method requires heating of reaction solution to a relatively high temperature (90-100 °C), can pose complication during large-scale preparation. Alternatively, the coprecipitation can be achieved using titration or coprecipitation at high supersaturation methods, using alkaline solutions. However, literature that describes alkali-induced coprecipitation for Ni-Ti LDH synthesis [8, 10] also describes the prolonged hydrothermal treatment as synthesis procedure which has complications similar to homogeneous coprecipitation.



But the effect of thermal treatment on the Ni-Ti LDH properties is poorly understood. Therefore the main aim of this paper was the comparative investigation of thermally treated and untreated Ni-Ti LDH samples, synthesized by a high supersaturation coprecipitation method.

2. MATERIALS AND METHODS

2.1 Reagents

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, TiCl_4 , NaOH , Na_2CO_3 , and HCl were analytical grade and were used as received.

2.2 Sample preparation

An aqueous solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.62 ml of $\text{TiCl}_4 \cdot \text{HCl}$ mixture (volume ratio 1:1, amount of Ti^{4+} is 0.0074 mol), the molar ratio of $\text{Ni}^{2+}/\text{Ti}^{4+}=5$, was dropwise added to a stirred aqueous solution containing 0.078 mol of NaOH and 0.0163 mol of Na_2CO_3 . After the addition, the precipitate was collected and labeled as sample A.

A second sample was prepared following the same procedure, but during coprecipitation, the $\text{NaOH} + \text{Na}_2\text{CO}_3$ solution was kept at 65 °C and after precipitation, the precipitate was aged in mother liquor under same conditions for 17h. This obtained sample was labeled as sample B.

2.3 Sample characterization

The prepared samples were characterized by means of Scanning Electron Microscopy (SEM) X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC).

SEM images were recorded using JEOL JSM-6510 Scanning Electron Microscope.

XRD patterns were recorded on Dron 3 diffractometer (Cu K α radiation, $\lambda=0.154$ nm) in range 5-85° 2 θ ; step 0.1 2 θ .

TGA was performed using Shimadzu DTG-60 under air atmosphere; heating rate 5 °C/min.

DSC was performed using Shimadzu DSC-60 under air atmosphere; heating rate 5°C/min.

3. RESULTS AND DISCUSSIONS

3.1 XRD analysis

Figures 1 and 2 shows XRD patterns of prepared samples, in comparison to the characteristic reflection of α - $\text{Ni}(\text{OH})_2$ and β - $\text{Ni}(\text{OH})_2$; and XRD patterns of Ni-Ti LD (not normalized), taken from literature [4].

According to the literature [28], synthesis of nickel hydroxide using precipitation at high supersaturation, leads to a formation of pure β - $\text{Ni}(\text{OH})_2$ phase. From Figures 1 and 2, it can be seen that both prepared samples demonstrate reflections at low 2 θ angles (12-13°) which are characteristic of α - $\text{Ni}(\text{OH})_2$ and Ni-Ti LDH. This indicates incorporation of titanium cations into the structure of nickel hydroxide with the formation of LDH structure. The disagreement in peak positions is attributed to the difference in interlayer distance and structural disorders.

When comparing XRD patterns of prepared samples, it can be seen that sample B (Figure-2) does not differ significantly from sample A (Figure-1), except for more defined reflections, indicating that higher synthesis temperature only affected crystallinity and morphology of the samples.

In the literature on Ni Ti LDH synthesis [8] using the mixture of NaOH and Na_2CO_3 , authors state that for molar ratio Ni: Ti 5:1 in the precursor solution, the formation of LDH phase was not observed. However, they used titanyl sulfate (TiOSO_4) as a source of Ti^{4+} cations, which implies the importance of metal cation source on LDH formation.

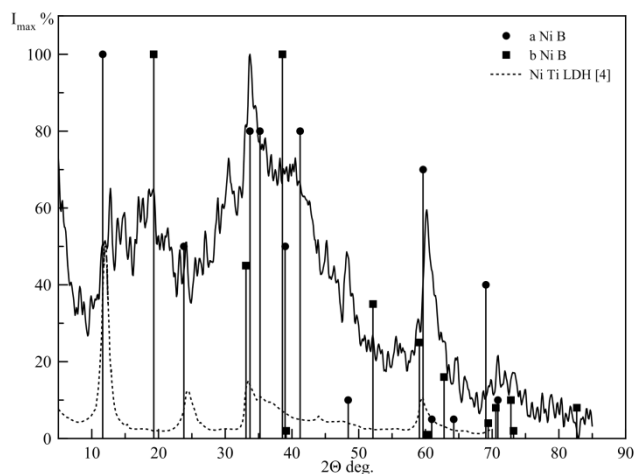


Figure-1. XRD pattern for sample A.

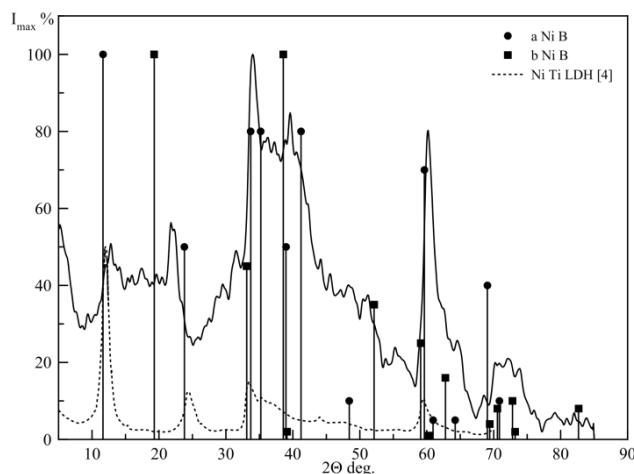


Figure-2. XRD pattern for sample B.

3.2 SEM analysis

Figures 3 and 4 show SEM images of the prepared samples.

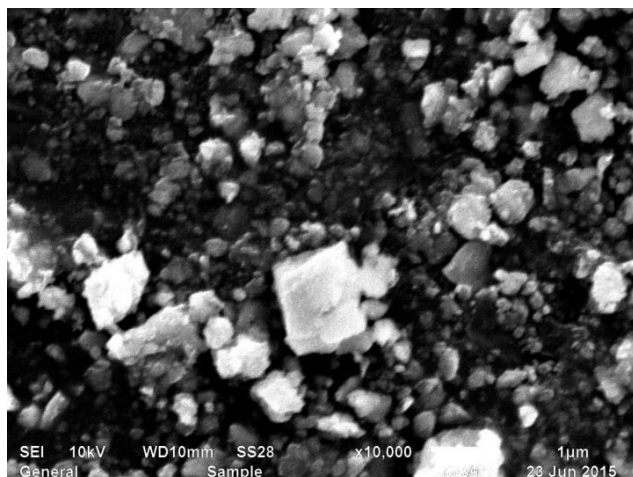


Figure-3. SEM image of sample A.

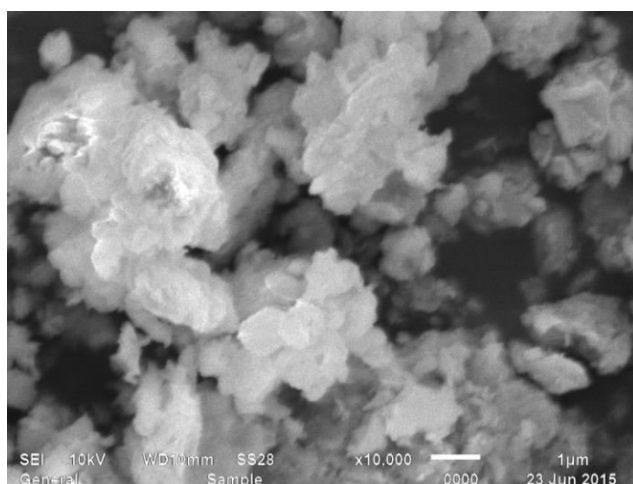


Figure-4. SEM image of sample B.

Both samples demonstrate the morphology of irregularly-shaped aggregates. However sample B (Figure. 4) demonstrate notably larger aggregate size, than sample A (Figure-3). This is in agreement with literature data [29] on the effect of hydrothermal treatment on LDH morphology.

3.3 TG-DSC analysis

Figures 5 and 6 show TG-DSC curves of prepared samples. It can be seen that thermal decomposition of both samples occur in two stages: 1) endothermic (below 170 °C, slow mass loss) - loss of adsorbed and interlayer water; 2) endothermic (261-336 °C, rapid mass loss) - loss of interlayer anions layer dehydroxylation, resulting into transformation of layered double hydroxide into layered double oxide (LDO).

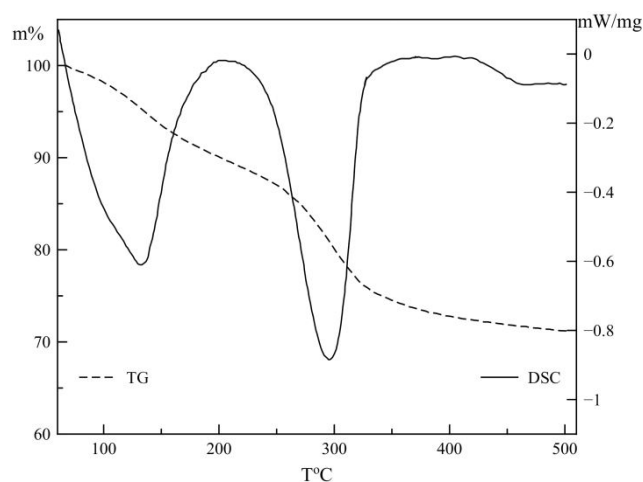


Figure-5. TG-DSC curves of sample A.

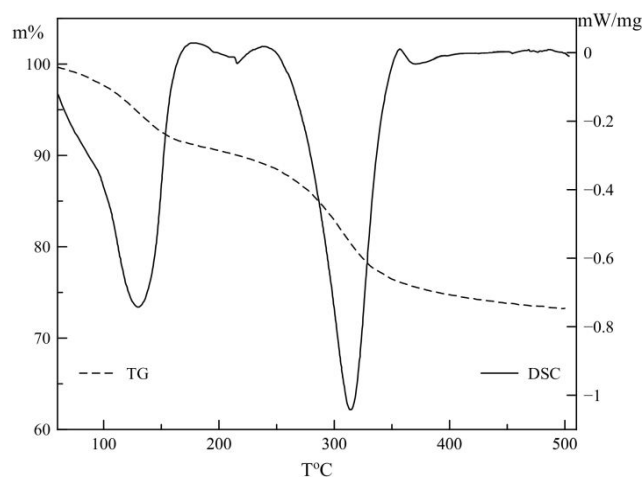
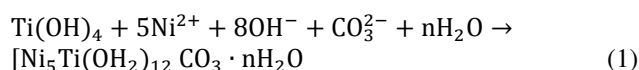


Figure-6. TG-DSC curves of sample B.

The second mass loss for sample A (Figure-5) starts at 261 °C and ends at 321 °C, while for sample B (Figure-6) it starts at 267 °C and ends at 336 °C, indicating higher thermal stability of the latter. This is explained by the difference in sample morphology: sample B is composed of larger aggregates, thermal decomposition of which requires higher temperatures. This demonstrates the positive effect of hydrothermal treatment on thermal stability of LDH.

3.4 Assumed formation mechanism

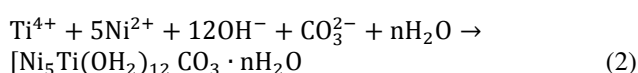
While describing the formation mechanism for Ni-Ti LDH during titration synthesis method [8] the authors proposed formation mechanism similar to M^{2+} - M^{3+} LDH [30]. They assume that formation of Ni-Ti LDH in two-stage: 1) formation of titanium hydroxide; 2) reaction of titanium hydroxide with nickel cations, hydroxyl groups, anions and water with formation of Ni-Ti LDH:





During titration, a gradual increase of pH leads to precipitation of titanium hydroxide. After all titanium hydroxide has been precipitated, further addition should lead to formation of $\text{Ni}(\text{OH})_2$, but in case of $\text{Ni}^{2+}/\text{Ti}^{4+}$ solution the precipitation of the second phase occurs at lower pH than precipitation of $\text{Ni}(\text{OH})_2$ from solution with same Ni^{2+} concentration, confirming formation of Ni-Ti LDH, instead of mixed titanium-nickel hydroxides.

In case of coprecipitation at high supersaturation, the pH of the reaction solution is sufficient for precipitation of both Ni^{2+} and Ti^{4+} from solution. Thus it can be assumed that stage corresponding to titanium hydroxide is either very fast or formation occurs in one stage:



4. CONCLUSIONS

Two hydroxide samples were prepared using coprecipitation at high supersaturation, using $\text{Ni}^{2+}/\text{Ti}^{4+}$ (molar ratio $\text{Ni}^{2+}/\text{Ti}^{4+}$ of 5/1) solution and $\text{NaOH}+\text{Na}_2\text{CO}_3$ solution. The prepared samples were characterizing XRD, SEM, TG and DSC analysis methods.

The XRD diffraction results showed that both prepared samples are Ni-Ti LDH. The SEM results showed that the morphology of both samples is constituted by irregularly-shaped agglomerates.

Results of TG and DSC showed that elevated synthesis temperature has the positive effect on thermal stability of prepared LDH. Ni-Ti LDH formation mechanism has been proposed during coprecipitation at high supersaturation.

REFERENCES

- [1] Cavani F. Trifiro F. Vaccari A. 1991. Hydrotalcite-type anionic clays: preparation, properties and applications. *Catalysis Today*. 11(2):173-301.
- [2] He J., Wei M., Li B., Kang Y., Evans D. G., Duan X. 2006. Preparation of Layered Double Hydroxides. In X. Duan & D. G. Evans (Eds.), *Layered Double Hydroxides*. Berlin/Heidelberg: Springer-Verlag. 119: 89-119.
- [3] Kovalenko V., Kotok V. 2017. Obtaining of Ni-Al layered double hydroxide by slit diaphragm electrolyzer. *Eastern European Journal of Enterprise Technologies*. 2(6-86): 11-17.
- [4] Scavetta E., Ballarin B., Corticelli C., Gualandi I., Tonelli D., Prevot V., Forano C. Mousty C. 2012. An insight into the electrochemical behavior of Co/Al layered double hydroxide thin films prepared by electrodeposition. *Journal of Power Sources*. 201: 360-367.
- [5] Yarger M. S., Steinmiller E. M. P., Choi K.-S. 2008. Electrochemical Synthesis of Zn-Al Layered Double Hydroxide (LDH) Films. *Inorganic Chemistry*. 47(13): 5859-5865.
- [6] Kovalenko V., Kotok V. 2017. Study of the influence of the template concentration on the properties of nickel hydroxide, obtained by homogeneous precipitation, for super capacitor application. *Eastern European Journal of Enterprise Technologies*. 4(6-88): 17-22.
- [7] Kovalenko V.L., Kotok V.A., Sykchin A.A., Mudryi I.A., Ananchenko B.A., Burkov A.A., Solovov V.A., Deabate S., Mehdi A., Bantignies J.-L., Henn F. 2017. Nickel hydroxide obtained by high-temperature two-step synthesis as an effective material for supercapacitor applications. *Journal of Solid State Electrochemistry*. 21(3): 683-691.
- [8] Zhang W. H., Guo X. D., He J., Qian Z. Y. 2008. Preparation of Ni(II)/Ti(IV) layered double hydroxide at high supersaturation. *Journal of the European Ceramic Society*. 28(8): 1623-1629.
- [9] Shu X., Zhang W., He J., Gao F., Zhu Y. 2006. Formation of Ni-Ti-layered double hydroxides using homogeneous precipitation method. *Solid State Sciences*. 8(6): 634-639.
- [10] Gao Z., Du B., Zhang G., Gao Y., Li Z., Zhang H., Duan X. 2011. Adsorption of Pentachlorophenol from Aqueous Solution on Dodecylbenzenesulfonate Modified Nickel-Titanium Layered Double Hydroxide Nanocomposites. *Industrial & Engineering Chemistry Research*. 50: 5334-5345.
- [11] Hu L.-F., Gao W., He J., Liu H., Li B., Zhang X.-M. 2013. NiTi-layered double hydroxide intercalated with β -CD and CM- β -CD: Interaction between the interlayer guests and the laminates. *Journal of Molecular Structure*. 1041: 151-155.
- [12] Lee Y., Choi J. H., Jeon H. J., Choi K. M., Lee J. W., Kang J. K. 2011. Titanium-embedded layered double hydroxides as highly efficient water oxidation photocatalysts under visible light. *Energy & Environmental Science*. 4(3): 914.
- [13] Zhao Y., Chen P., Zhang B., Su D. S., Zhang S., Tian L., Lu J., Li Z., Cao X., Wang B., Wei M., Evans D.G., Duan X. 2012. Highly Dispersed TiO_6 Units in a Layered Double Hydroxide for Water Splitting. *Chemistry*. 18(38): 11949-11958.



- [14] Zhao Y., Li B., Wang Q., Gao W., Wang C. J., Wei M., Evans D.G., Duan X., O'Hare D. 2014. NiTi-Layered double hydroxides nanosheets as efficient photocatalysts for oxygen evolution from water using visible light. *Chem. Sci.* 5(3): 951-958.
- [15] Solovov V., Kovalenko V., Nikolenko N., Kotok V., Vlasova E. 2017. Influence of temperature on the characteristics of Ni(II), Ti(IV) layered double hydroxides synthesized by different methods. *Eastern-European Journal of Enterprise Technologies.* 1(6-85): 6-22.
- [16] Faour A., Mousty C., Prevot V., Devouard B., De Roy A., Bordet P., Elkaim E., Taviot-Gueho C. 2012. Correlation among Structure, Microstructure, and Electrochemical Properties of NiAl-CO₃ Layered Double Hydroxide Thin Films. *The Journal of Physical Chemistry C.* 116(29): 15646-15659.
- [17] Kovalenko V., Kotok V. 2017. Definition of effectiveness of β -Ni(OH)₂ application in the alkaline secondary cells and hybrid supercapacitors. *Eastern-European Journal of Enterprise Technologies.* 5(6-89): 17-22.
- [18] Hu M., Gao X., Lei L., Sun Y. 2009. Behavior of a Layered Double Hydroxide under High Current Density Charge and Discharge Cycles. *The Journal of Physical Chemistry C.* 113(17): 7448-7455.
- [19] Kovalenko V., Kotok V. 2018. Comparative investigation of electrochemically synthesized (α + β) layered nickel hydroxide with mixture of α -Ni(OH)₂ and β -Ni(OH)₂. *Eastern European Journal of Enterprise Technologies.* 2(6-92): 16-22.
- [20] Shangguan E., Li J., Guo D., Guo L., Nie M., Chang Z., Yuan X., Wan, H. A. 2015. Comparative study of structural and electrochemical properties of high-density aluminum substituted α -nickel hydroxide containing different interlayer anions. *Journal of Power Sources.* 282: 158-168.
- [21] Kovalenko V., Kotok V. 2018. Influence of ultrasound and template on the properties of nickel hydroxide as an active substance of supercapacitors. *Eastern-European Journal of Enterprise Technologies.* 3(12-93): 32-39.
- [22] Kotok V., Kovalenko V. 2017. Electrochromism of Ni(OH)₂ films obtained by cathode template method with addition of Al, Zn, Co ions. *Eastern European Journal of Enterprise Technologies.* 3(12-87): 38-42.
- [23] Kotok V.A., Kovalenko V.L., Kovalenko P.V., Solovov V.A., Deabate S., Mehdi A., Bantignies J.L., Henn F. 2017. Advanced electrochromic Ni(OH)₂/PVA films formed by electrochemical template synthesis. *ARPJ Journal of Engineering and Applied Sciences.* 12(13): 3962-3977.
- [24] Debajyoti M., Gilles V. 2012. Improved reversibility of color changes in electrochromic Ni-Al layered double hydroxide films in presence of electroactive anions. *Journal of Electroanalytical Chemistry.* 687: 58-63.
- [25] Vidotti M., van Greco C., Ponzio E. A., Córdoba de Torresi S. I. 2006. Sonochemically synthesized Ni(OH)₂ and Co(OH)₂ nanoparticles and their application in electrochromic electrodes. *Electrochemistry Communications.* 8(4): 554-560.
- [26] Hall D. S., Lockwood D. J., Bock C., MacDougall B. R. 2014. Nickel hydroxides and related materials: a review of their structures, synthesis and properties. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences.* 471(2174): 20140792-20140792.
- [27] Kovalenko V., Kotok V., Yeroshkina A., Zaychuk A. 2017. Synthesis and characterization of dyeintercalated nickel-aluminium layered double hydroxide as a cosmetic pigment. *Eastern-European Journal of Enterprise Technologies.* 5(12-89): 27-33.
- [28] Ramesh T. N., Kamath P. V. 2006. Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder. *Journal of Power Sources.* 156(2): 655-661.
- [29] Oh J. 2002. The effect of synthetic conditions on tailoring the size of hydrotalcite particles. *Solid State Ionics.* 151(1-4): 285-291.
- [30] Bocclair J. W., Braterman P. S. 1999. Layered Double Hydroxide Stability. 1. Relative Stabilities of Layered Double Hydroxides and Their Simple Counterparts. *Chemistry of Materials.* 11(2): 298-302.