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INFLUENCE OF TEMPERATURE ON THE CHARACTERISTICS OF Ni(II), Ti(IV) LAYERED DOUBLE HYDROXIDES SYNTHESISED BY DIFFERENT METHODS

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Ni(II) – Ti(IV) шарові подвійні гідроксиди були синтезовані методами прямого, зворотнього та гомогенного осадження. Отримані зразки були охарактеризовані за допомого ренгенофазового аналізу, термогравіметрії та диференціальної скануючої калориметрії. За даними РФА було встановлено, що отримані зразки мають структуру подвійного-шарового гідроксиду. Було проведено порівняння характеристик отриманих зразків

Ключові слова: подвійно-шаровий гідроксид, нікель, титан, прямее осадження, зворотнэ осадженняб гомогеннее осадження

Ni(II) – Ti(IV) слоистые двойные гидроксиды были синтезированы методами прямого, обратного и гомогенного осаждения. Полученные образцы были охарактеризованы при помощи рентгенофазового анализа (РФА), термогравиметрии (ТГ) и дифференциальной сканирующей калориметрии (ДСК). По данным РФА было установлено, что полученные образцы имеют структуру слоистого двойного гидроксида. Было проведено сравнение характеристик полученных образцов

Ключевые слова: слоистый двойной гидроксид, никель, титан, прямое осаджение, обратное осаждение, гомогенное осаждение

1. Introduction

Layered double hydroxides (LDH) or hydrotalcite-like compounds are a class of natural and synthetic compounds with the general formula

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/m}]^{m-}\cdot nH_2O,$$

where M^{2+} is 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^- etc.). They have layered structure similar to brucite ($Mg(OH)_2$), in which part of divalent cations is substituted by trivalent ones. Such substitution creates an excessive positive charge, which is compensated by anions that reside in the interlayer space along with water [1]. LDH with tetravalent cations such as Ti^{4+} [2, 3], Zr^{4+} [4], V^{4+} [5] are also described in the literature.

Ni–Ti LDH, which can also be characterized as titanium-stabilized α-$Ni(OH)_2$, are widely used in the same fields as nickel hydroxide:

a) as electrode materials for power sources, such as lamellar alkaline accumulators [6, 7], supercapacitors with composite [8] or individual film electrodes [9], supercapacitors and alkaline accumulators with pasted electrodes [10];

b) as electrochromic films for devices based on nickel hydroxide [11], Ni–Al LDH [12], Ni LDH with various cations [13];

c) as a catalyst for electrooxidation of various organic compounds [14], including methanol [15, 16].

It should be noted that LDHs have significant advantages over pure $Ni(OH)_2$. For instance, when used in supercapacitors, Ni–Ti LDH demonstrates higher specific capacity than $Ni(OH)_2$ [9]. Ni–Ti LDH can be used as a photocatalyst [17, 18], electrode material for photoelectrochemical cells [19], anion sorbents [20], precursors for mixed oxide systems [21, 22]. Nickel-titanium LDH can be used for removal of organic pollutants from water. In particular for full electrooxidation of formaldehyde, that is formed during production of phenol-formaldehyde resins and materials based on them [23].

The application range of LDH can be further increased by introduction of various functional anions into the interlayer space. For instance, introduction of molybdate [24] or peroxotitanate anion [25] allows to obtain effective oxidation catalysts. Introduction of polyoxotungstate anion into the interlayer space allows to obtain a propene epoxidation catalyst [26] or photooxidation catalyst [27].

Introduction of hexacyanoferrate ions into the structure of Ni–Ti LDH allows for its application as a sorbent for ^{137}Cs [28].

Based on previous statements, the development of an optimal synthesis method of LDH, Ni-Ti particularly, is a relevant problem.

2. Literature review and problem statement

Nickel hydroxide and LDH can be prepared using various methods, for instance: high-temperature two-stage synthesis [29], electrochemically in a slit-diaphragm electrolyzer [30], decomposition method [31], precipitation at constant pH [32, 33], high-temperature interaction of solution with nickel-foam matrix [38]. The most common and simple is chemical precipitation at various temperatures. Additionally, hydrothermal treatment, i. e. precipitate ageing in mother liquor at constant stirring at set temperature can be carried out. The precipitation can be conducted using various methods:

a) *Titration method*. The procedure is carried out by fractional addition of a basic solution (NaOH, KOH) to metal salt solution (Me^{2+} and Me^{3+}) [4, 32, 37]. In the work [4] the precipitation is carried out at room temperature, however, the hydrothermal treatment at 100 °C has been conducted after precipitation. The paper [32] describes precipitation using titration method at 85–90 °C. The work [37] describes the synthesis of Ni-Al LDH using LiOH solution at 100 °C, with hydrothermal post-treatment at 100 °C during 10 hours and at 180 °C during 1 day. However, none of the listed papers present a rationale behind such synthesis temperatures.

b) *Coprecipitation at high supersaturation*. The procedure is carried out by addition of a salt solution (Me^{2+} and Me^{3+}) to a basic solution (NaOH, KOH). This method has been used for preparation of Co–Zr [4], Co–V [5]. The synthesis temperature was 65–85 °C. The rationale behind synthesis temperature is also not presented in the described works.

c) *Homogeneous coprecipitation method*. During homogeneous coprecipitation, the metal salt solution (M^{2+} and M^{3+}) with addition of amine compound is heated to the amine hydrolysis temperature. Hydrolysis causes basification of the solution's volume, causing precipitation process. The work [19] describes homogeneous coprecipitation using hexamethylenetetramine at 95 °C for preparation of various LDHs. However, urea is most commonly used for homogeneous coprecipitation, with synthesis temperatures of 90–100 °C [2, 17]. The precipitation temperature is defined by hydrolysis process, with higher temperatures increasing its rate. However, the possibility of conducting homogenous coprecipitaiton at temperatures below 90 °C has not been studied.

For synthesis of Ni–Ti LDH, the homogeneous coprecipitation at 100 °C [2, 20] and 90 °C [17, 34] is most frequently described. Homogeneous coprecipitation at 90 °C can also be used for preparation of composites based on Ni–Ti LDH, such as Ni–Ti LDH/reduced graphene [18] or Ni–Ti LDH/graphene [19]. Additionally, the paper [3] describes the preparation of Ni–Ti LDH using titration method, however, the hydrothermal treatment at 100–150 °C has been carried out after coprecipitation. It should be noted, that influence of synthesis conditions on Ni–Ti LDH has not been studied in detail. The choice of synthesis temperature has been almost arbitrary.

The main disadvantage of the presented method for synthesis of Ni–Ti LDH is utilization of high temperature during synthesis and hydrothermal treatment. For industrial application, the synthesis is preferred to conduct at the lowest possible temperature, in order to minimize power consumption. Thus, studying the influence of temperature on properties of Ni–Ti LDH and establishing the possibility of synthesis at a lower temperature is very relevant.

3. Aim and objectives

The aim of the work is to establish the influence of synthesis temperature on characteristics of Ni–Ti LDH, prepared using titration, coprecipitation at high supersaturation and homogeneous coprecipitation methods.

In order to achieve the set-out aim, the following objectives have been formulated:

– to synthesize Ni–Ti LDH using titration, coprecipitation at high supersaturation and homogeneous coprecipitation methods at different temperatures;

– to study the structure and composition of prepared Ni–Ti LDH samples;

– to establish the possibility of Ni–Ti LDH synthesis at lower temperatures for each synthesis method.

4. Synthesis and analysis methods of Ni–Ti LDH samples

4. 1. Synthesis of Ni-Ti LDH samples

Titration method. A solution containing 0.078 moles of NaOH and 0.0163 moles of Na_2CO_3 has been added drop-wise into a solution containing 0.037 moles of $Ni(NO_3)_2{\cdot}6H_2O$ and 1.62 ml of $TiCl_4$ and HCl mixture (volume ratio 1:1, 0.81 moles of Ti^{4+}) under stirring. After the final portion has been added, the reaction mixture has been aged at synthesis temperature under constant stirring during 17 hours. Two samples have been prepared at the following temperatures:

1) 65 °C. The sample has been labeled as Ni–Ti-THT (T – titration, HT – hydrothermal treatment);

2) 20 °C. The sample has been labeled as Ni–Ti-T.

Coprecipitation at high supersaturation. A solution containing 0.037 moles of $Ni(NO_3)_2{\cdot}6H_2O$ and 1.62 ml of $TiCl_4$

and HCl mixture (volume ratio 1:1, 0.81 moles of Ti^{4+}) has been added drop-wise into a solution containing 0.078 moles of NaOH and 0.0163 moles of Na_2CO_3 under stirring. After the final portion has been added, the reaction mixture has been aged at synthesis temperature under constant stirring during 17 hours. Two samples have been prepared at the following temperatures:

1) 65 °C. The sample has been labeled as Ni–Ti-HSHT (HS – high supersaturation, HT – hydrothermal treatment);

2) 20 °C. The sample has been labeled as Ni–Ti-HT.

Homogeneous coprecipitation. 24.05 g of urea has been added to a solution containing 0.037 moles of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.62 ml of $TiCl_4$ and HCl mixture (volume ratio 1:1, 0.81 moles of Ti^{4+}). The obtained solution has been kept at 70 °C or 80 °C during 5 h. The obtained samples have been labeled as Ni–Ti-HC70 (HC – homogeneous coprecipitation) and Ni–Ti-HC80 accordingly.

In all cases, the prepared samples have been filtered, dried at 65 °C, ground, sifted through a 71 μm nickel mesh, washed with distilled water and dried again.

4. 2. Analysis methods of Ni–Ti LDH samples

The samples have been analyzed using XRD, TG and DSC. The XRD patterns have been recorded on Dron 3 diffractometer (Cu Kα) in the range 5–85° 2θ. TG analysis has been conducted using thermal analyzer Shimadzu DTG-60 in air, heating rate 5 °C/min. DSC analysis has been conducted using differential scanning calorimeter Shimadzu DSC-60 in air, heating rate 5 °C/min.

5. Results of sample analysis

Fig. 1–6 show XRD patterns of prepared samples. For a comparison, they also show characteristic reflection for α-$Ni(OH)_2$, β-$Ni(OH)_2$, and XRD of Ni-Ti LDH prepared using homogeneous coprecipitation, taken from the literature [2]. Reflection corresponding to β-$Ni(OH)_2$ and α-modification, which is characteristic of the LDH structure, can be observed on XRD patterns of Ni–Ti-THT (Fig. 1) and Ni–Ti-T (Fig. 2) samples. The obtained data is in a good agreement with the literature. It should be noted that crystallinity of Ni–Ti-T sample is lower.

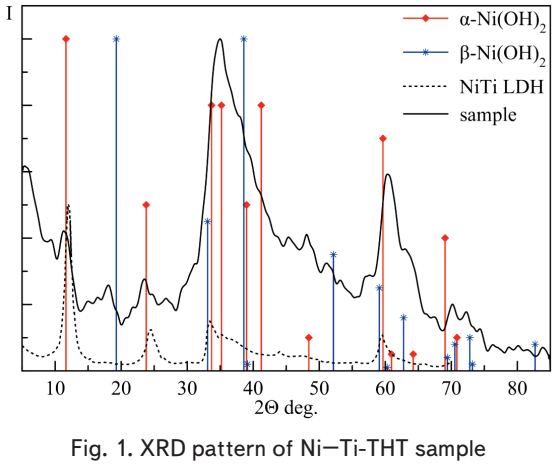

Fig. 1. XRD pattern of Ni—Ti-THT sample

Ni–Ti-HSHT (Fig. 3) and Ni–Ti-HS (Fig. 4) samples demonstrate a structure similar to samples Ni–Ti–THT and Ni–Ti-T correspondingly.

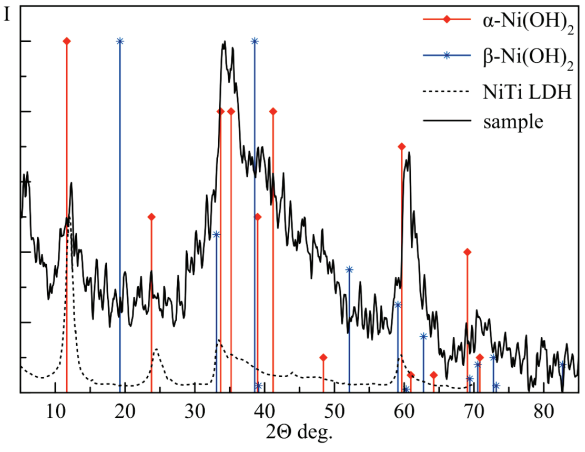

Fig. 2. XRD pattern of Ni—Ti-T sample

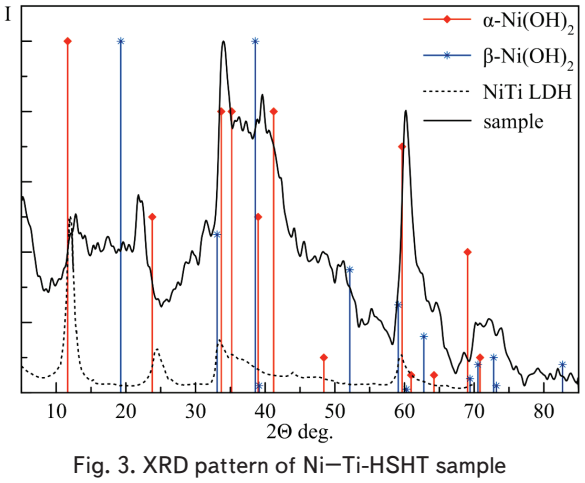

Fig. 3. XRD pattern of Ni—Ti-HSHT sample

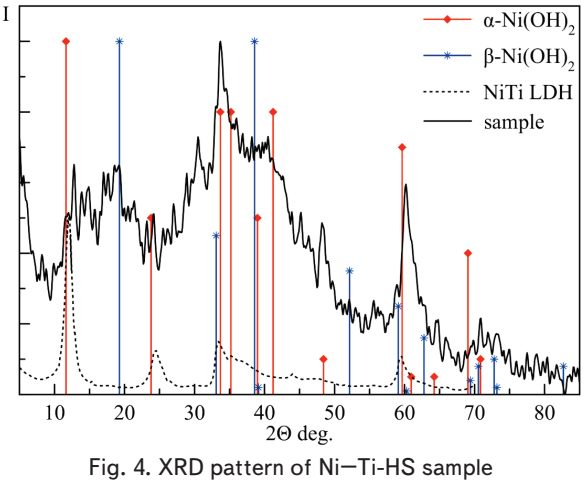

Fig. 4. XRD pattern of Ni—Ti-HS sample

Unlike previous samples, the Ni–Ti-HC70 (Fig. 5) and Ni–Ti-HC80 (Fig. 6) samples demonstrate significantly different structures. Homogeneous coprecipitation at 70 °C results in preferential formation of β-$Ni(OH)_2$, while in case of homogeneous coprecipitation at 80 °C the α-structure is preferred.

Fig. 7–12 show TG-DSC patterns of prepared samples. For samples prepared using titration (Fig. 7, 8) and coprecipitation at high supersaturation methods, 2 mass loss steps can be highlighted:

1) ~100–150 °C;

2) ~270–340 °C.

Two corresponding endothermic peaks can be observed on DSC curve.

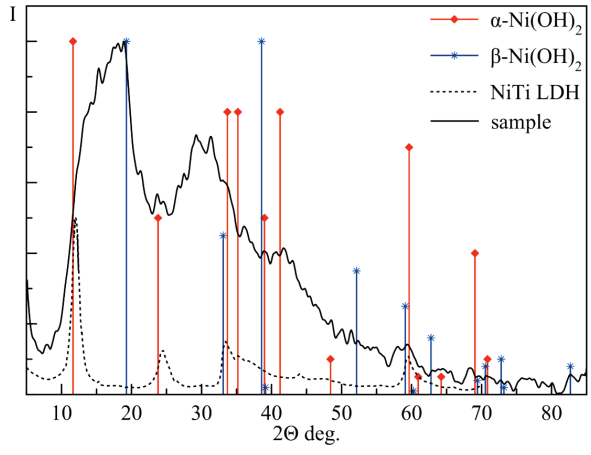

Fig. 5. XRD pattern of Ni—Ti-HC70 sample

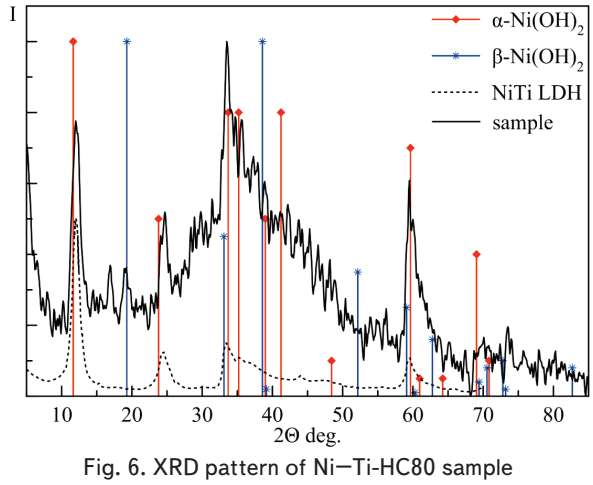

Fig. 6. XRD pattern of Ni—Ti-HC80 sample

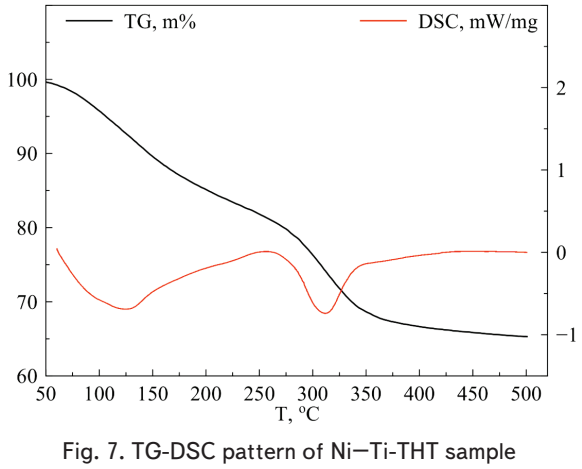

Fig. 7. TG-DSC pattern of Ni—Ti-THT sample

For samples prepared using homogeneous coprecipitation, Ni–Ti-HC70 (Fig. 11) and Ni–Ti-HC80 (Fig. 12), two mass loss steps can also be observed on TG curve, however, the mass loss on the first step is sufficiently lower than for titration and coprecipitation at high supersaturation samples.

DSC curve for homogeneous coprecipitation samples has a fundamentally different form. The first endothermic peak is almost absent, and a sharp exothermic peak can be observed in a temperature region of the second mass loss.

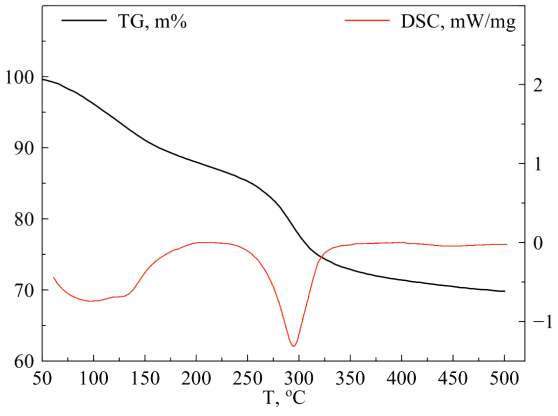

Fig. 8. TG-DSC pattern of Ni—Ti-T sample

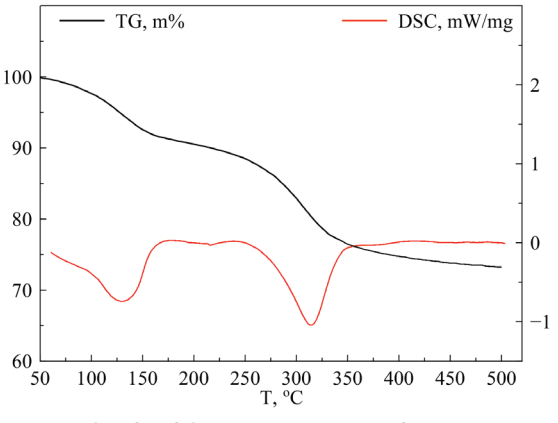

Fig. 9. TG-DSC pattern of Ni—Ti-HSHT sample

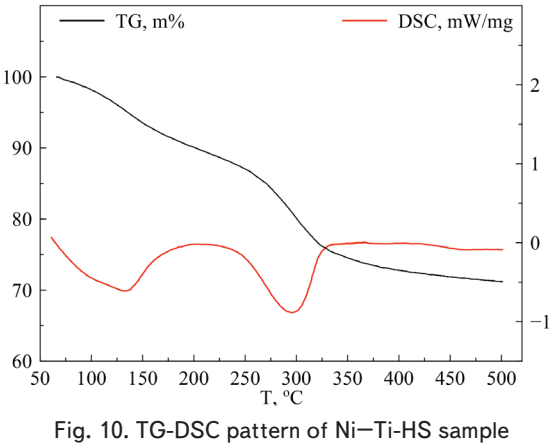

Fig. 10. TG-DSC pattern of Ni—Ti-HS sample

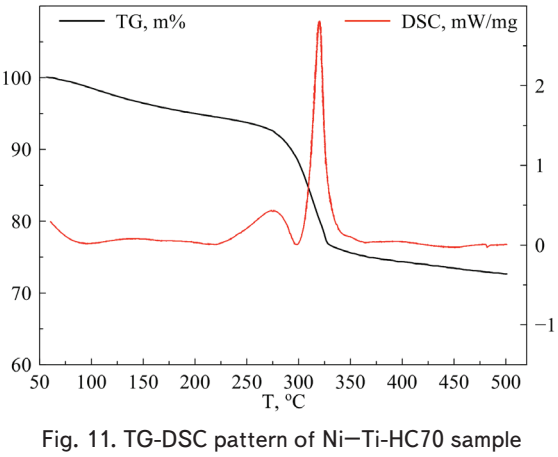

Fig. 11. TG-DSC pattern of Ni—Ti-HC70 sample

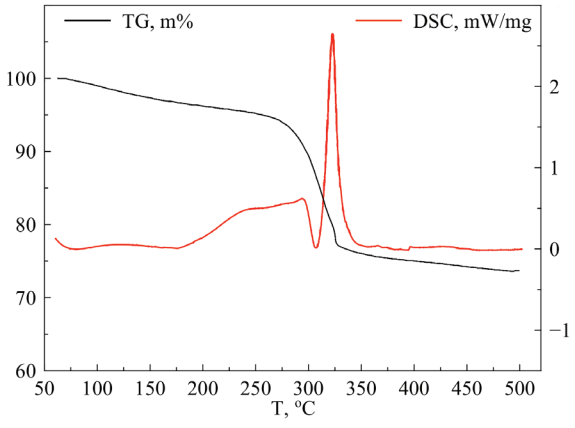

Fig. 12. TG-DSC pattern of Ni—Ti-HC80 sample

6. Discussion of analysis results for Ni–Ti LDH samples synthesized by different methods at different temperatures

6. 1. Study of Ni–Ti LDH samples using X-ray diffraction analysis

It should be noted that no reflection of titanium oxides or oxyhydroxides can be observed on XRD patterns of prepared samples, proving the formation of Ni–Ti LDH. Ni–Ti LDH samples prepared using titration and coprecipitation at high supersaturation method, demonstrate reflections at ~12° (001 plane of α-$Ni(OH)_2$) and at ~19° (001 plane of β-$Ni(OH)_2$). The intensity of reflection corresponding to β-modification is lower than that of α-modification. This indicates there is some small amount of β-$Ni(OH)_2$ phase in the samples. A sharp intensity increase in the region of small angles can be observed on XRD patterns, which indicates the presence of an amorphous phase. Synthesis and hydrothermal treatment at elevated temperature (65 °C) lead to intensity decrease of reflection corresponding to β-modification. Thus, with elevated temperature, the amount of β-$Ni(OH)_2$ impurity is decreased. Samples prepared at a higher temperature (Ni–Ti-HSHT and Ni–Ti-THT) have higher crystallinity.

It should be noted that XRD pattern of Ni–Ti-HC80 (Fig. 6) is similar to patterns of Ni–Ti-THT (Fig. 1) and Ni–Ti-T (Fig. 2). Such similarity is related to the gradual basification of solution during urea hydrolysis, (reactions 1–4) [35], which is also characteristic of titration method:

$$(NH_2)CO \rightarrow NH_4CNO, \quad (1)$$

$$NH_4CNO \leftrightarrow NH_4^+ + CNO^-, \quad (2)$$

$$NH_4CNO \rightarrow 2NH_3 + CO_2, \quad (3)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-. \quad (4)$$

In case of homogeneous coprecipitation, synthesis at 70 and 80 °C leads to fundamentally different structures of the samples. In case of the Ni–Ti-HC70 sample (Fig. 5), the highest intensity is observed for reflection at 19°, which is characteristic of β-$Ni(OH)_2$ phase. It is likely tied to the fact that ammonia formed during the reaction (3) forms a soluble complex with nickel:

$$6NH_3 + Ni^{2+} \leftrightarrow [Ni(NH_3)_6]^{2+}. \quad (5)$$

Formation of this complex reduced the rate of nickel precipitation, preventing its incorporation into the LDH structure which leads to formation of a separate phase of β-$Ni(OH)_2$:

$$[Ni(NH_3)_6]^{2+} + 2OH^- \rightarrow 6NH_3 + \beta\text{-}Ni(OH)_2. \quad (6)$$

Sample Ni–Ti-HC80 shows very weak β-$Ni(OH)_2$ reflections, but intensities of α-modification reflection are strong. Thusly, during homogeneous coprecipitation at 80 °C formation of Ni–Ti LDH is preferred. This effect can be explained by a higher hydrolysis rate of urea at higher temperatures, leading to a higher rate pH increase and as a result the influence of ammonia on precipitation process is diminished.

6. 2. Study of Ni-Ti LDH samples using thermogravimetry and differential scanning calorimetry methods

Thermal decomposition of samples prepared using titration and coprecipitation at high supersaturation methods (Fig. 7–10) occurs in two stages:

1) an endothermic event (100–150 °C), accompanied by a sharp mass loss, related to the loss of interlayer and crystallization water;

2) an endothermic event (260–350 °C), which is also accompanied by a sharp mass loss and related to the loss of interlayer anions (carbonates) and water loss during decomposition of the crystal lattice of layered double hydroxide with its transformation into layered double oxide (LDO). Such TG and DSC curves are characteristic of α-$Ni(OH)_2$ and nickel-based LDH.

It should be noted that for Ni–Ti-THT and Ni–Ti-T samples, decomposition of LDH lattice with transformation into LDO occurs at higher temperatures (280.4 °C and 270.8 °C), than for Ni–Ti-HSHT and Ni–Ti-HS samples (267.12 °C and 261.4 °C), which indicated higher stability of the crystal lattice. The data presented indicate that higher synthesis temperatures improve the stability of the sample's crystal lattice.

For samples prepared using homogeneous coprecipitation (Fig. 11, 12), the endothermic effect corresponding to the loss of interlayer water is almost absent on the DSC curve. In addition, two exothermic effects in the 180–350 °C range can be observed. The TG curves demonstrated two mass loss steps as for other samples, including the mass loss step that corresponds to the decomposition of LDH lattice with transformation into LDO. It is known that the latter process is endothermic, however, the endothermic peak is absent on the DSC curve (Fig. 11, 12), and a significant exothermic peak can be observed instead. The most likely explanation is that in this temperature range not one but few processes with different values of thermal effects occur, resulting in a competition of exo- and endothermic effect.

In the work [2] the assumed exothermic process is described as oxidation of cyanate anion that has been formed during the reaction (2) and incorporated into the interlayer space of LDH for compensation of excessive cationic charge. The peak at 375–385 °C likely corresponds to oxidation of cyanate-anion. However, with this process alone the absence of the first endothermic event cannot be explained. Based on data for urea pyrolysis [36], an assumption can be made that up to 280 °C exothermic transformation of cyanate occurs, compensating endothermic effect from the loss of interlayer water, followed by complete oxidation of the formed com-

pound at higher temperatures, simultaneously with transformation of LDH into LDO.

7. Conclusions

1. Based on XRD results, it has been revealed that Ni-Ti LDH samples prepared using titration and coprecipitation at high supersaturation methods at 65 °C and 20 °C have the structure of layered double hydroxide. A small amount of β-$Ni(OH)_2$ impurity has been found. Increasing the temperature of synthesis and hydrothermal treatment increases crystallinity and thermal stability of the LDH structure, while reducing the content of β-modification.

2. By means of DSC it has been demonstrated that during homogeneous coprecipitation at 70 °C and 80 °C the cyanate-containing Ni–Ti LDH is formed. According to XRD results, homogeneous coprecipitation at 70 °C leads to a significant content of β-$Ni(OH)_2$ in the precipitate. Increasing the synthesis temperature up to 80 °C lead to the almost complete disappearance of β-$Ni(OH)_2$ reflection from XRD pattern, indicating preferred formation of Ni–Ti.

3. Synthesis of Ni–Ti LDH using titration and coprecipitation at high supersaturation can be conducted at low temperatures (20 °C). However, high temperatures (80 °C or higher) are required for synthesis of Ni–Ti LDH using homogeneous coprecipitation.

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