



# Article Layered Double Hydroxide-Derived Ni-Mg-Al Catalysts for Ammonia Decomposition Process: Synthesis and Characterization

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**Abstract:** Layered Ni-Mg-Al hydroxides with (Ni + Mg)/Al = 2.5 differing in Mg/Ni ratios and related oxide systems have been synthesized and characterized. Ni-Mg-Al hydroxides were prepared by the coprecipitation method. It was found that the samples dried at 110 °C were layered Ni-Mg-Al hydroxides with a hydrotalcite-type structure. After the heat treatment at 600 °C, the formation of Ni-Mg-Al-mixed oxides with a specific nanostructure, an intermediate between a NaCl and spinel structure, took place. According to XRD data, it had the unit cell parameter a = 4.174–4.181 Å, and a crystallite size of 4.0 nm. The specific surface area of the Ni-Mg-Al samples dried at 110 °C was 45–54 m<sup>2</sup>/g, and that of those calcined at 600 °C was 156.1–209.1 m<sup>2</sup>/g. In agreement with HRTEM data, in all the synthesized nickel catalysts reduced at 700 °C (H<sub>2</sub>), particle size was mainly distributed between 15–20 nm. The catalyst activity of LDH-derived Ni-Mg-Al catalysts in ammonia decomposition was studied in a fixed-bed flow-type reactor at an atmospheric pressure within the temperature range 500–700 °C. The synthesized catalysts overcame existing analogues in catalytic performance. At a process temperature of 500 °C, the Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT catalyst showed that the H<sub>2</sub> productivity was 23.8 mmol/(g<sub>cat</sub>·min), exceeding the respective value of nickel catalysts reported in the literature.

**Keywords:** nickel catalysts; hydrotalcite-derived catalysts; Ni-Mg-Al-double layered hydroxides Ni-Mg-Al mixed oxide; ammonia decomposition; H<sub>2</sub> production

## 1. Introduction

Recently, hydrogen has been considered a promising, environmentally benign power source for a variety of applications including fuel cell-based technologies in the energy and transport sectors. However, the specific physical properties of hydrogen (its low volumetric energy density, low boiling point, etc.) impose some restrictions on its storage and transportation and thus impede its wide practical application. This problem can be solved by using the so-called hydrogen carrier compounds (ammonia, methanol, dimethyl ether, etc.), which are safe for storing and transportation, and can easily release hydrogen, even on board a vehicle [1,2].

Within the concept of energy storing and transportation in a form of chemical compound, ammonia is considered the most promising option as it has high hydrogen content (~17.6%) and outperforms other hydrogen carriers in energy density, availability, and the ability to become liquefied and to be decomposed to release hydrogen [1,3–5]. Moreover, ammonia decomposition technology yields hydrogen with near zero carbon content [6].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The catalytic process of ammonia decomposition is a promising technology for hydrogen production. Intensive works are focused on the research and development of highly efficient catalysts for this process. It was found that the best ammonia decomposition catalysts include ruthenium supported by various materials [7–9]. However, ruthenium is an expensive scarce metal and therefore is hardly suitable for commercial use as a catalyst. Appropriate alternatives to ruthenium catalysts are nickel ones, as they demonstrate sufficient activity for the process of ammonia decomposition and are widely available for industry applications [6,10–13].

An analysis of the literature data allows the conclusion that the key factors affecting the characteristics of nickel catalysts are the dispersion of the active component, texture, and morphology, and the interaction of the active metal particles with support. Preferable supports for nickel catalysts are oxide materials with a high specific surface area, such as Al<sub>2</sub>O<sub>3</sub> [11,14,15], MgO [6,14,16], ZrO<sub>2</sub> [14,17], TiO<sub>2</sub> [6,14], CeO<sub>2</sub> [18], La<sub>2</sub>O<sub>3</sub> [6,14,16,19–21], mixed oxides ZrO<sub>2</sub>-CeO<sub>2</sub> [20–22], Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> [11,18,23], Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> [11], etc. According to the literature data, MgO is the most feasible support, since it possesses high basicity and thermal stability, and easily forms solid solutions with nickel oxide that facilitate the formation of dispersed nickel crystallites and thus promote the catalytic properties of nickel catalysts [24,25]. Traditionally, nickel catalysts are prepared by impregnation [6,11,14,15,17,22], or coprecipitation [20,21,23,26] methods.

Currently, promising materials for the process of ammonia decomposition are headed by hydrotalcites—a group of compounds with a basic character (also known as layered double hydroxides (LDH)), which attract much attention owing to their specific structure and suitability for a wide range of applications, such as catalysts, sorbents, precursors of mixed metal oxide catalysts, etc. [27–32]. Upon calcination, the LDH compound forms a homogeneous mixture of oxides characterized by small crystal size, high specific surface area, basic properties, and a uniform distribution of metal ions. The composition of the most common LDHs is described by the general formula  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal cations in brucite-like layers  $(M^{2+} = Mg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, etc.; M^{3+} = Al^{3+}, Fe^{3+}, etc.)$ , and  $A^{n-}$  is the interlayer compensating anion [33]. The types of metal cations, the  $M^{2+}/M^{3+}$  molar ratios, and the nature of interlayer compensating anions in LDH can vary widely, which facilitates the production of a great number of materials with different physical and chemical properties.

The present work is the first part of the research, in which a set of physicochemical methods (X-ray diffraction (XRD), transmission electron microscopy (TEM), lowtemperature nitrogen adsorption, thermal gravimetric analysis (TGA) and differential thermal analysis (DTA)) were used to characterize the nickel catalysts synthesized from LDHs with a hydrotalcite structure. The catalytic properties of the obtained nickel catalysts were studied in the process of ammonia decomposition.

#### 2. Results and Discussion

According to the elemental analysis data, in the  $Ni_xMg_yAl_2$ -HT samples with a given molar ratio, the contents of nickel oxide were 22.5, 28.4, 33.8, and 43.4 wt.%, which are quite close to the calculated values (Table 1). The Na content in the samples was below 0.003 wt.%, which indicates that the precipitates were well-washed during synthesis.

Figure 1a presents the XRD patterns of as-prepared  $Ni_xMg_yAl_2$ -HT catalysts dried at 110 °C. All diffraction peaks correspond to the LDH phase with the hydrotalcite structure. No other phase was observed that indicates the isomorphic replacement of  $Mg^{2+}$  cations by  $Ni^{2+}$  and  $Al^{3+}$  cations in brucite layers [34]. The unit cell parameters and CSR size (D) of the obtained samples are presented in Table 1.

|   | NiO Content, ••<br>wt.% |       | 110 °C             |               |                  |                      |                    | 600 °C             |       |       |
|---|-------------------------|-------|--------------------|---------------|------------------|----------------------|--------------------|--------------------|-------|-------|
| Sample  |                         |       | S <sub>BET</sub> , | Unit<br>Parar | t Cell<br>neters | s D <sub>001</sub> , | D <sub>110</sub> , | S <sub>BET</sub> , | a, nm | D, nm |
|   | Exp.                    | Calc. | m-/g               | a, Å          | c, Å             | nm                   | nm                 | m <sup>-</sup> /g  |       |       |
| NiMg <sub>4</sub> Al <sub>2</sub> -HT                   | 22.5                    | 22.1  | 52.7               | 3.048         | 23.036           | 8.5                  | 13.0               | 209.1              | 4.181 | 4.0   |
| Ni <sub>1.3</sub> Mg <sub>3.7</sub> Al <sub>2</sub> -HT | 28.4                    | 27.9  | 46.9               | 3.047         | 23.045           | 8.0                  | 12.0               | 189.5              | 4.179 | 4.0   |
| Ni <sub>1.6</sub> Mg <sub>3.4</sub> Al <sub>2</sub> -HT | 33.8                    | 33.2  | 52.1               | 3.047         | 23.089           | 8.0                  | 11.0               | 179.8              | 4.174 | 4.0   |
| Ni <sub>2</sub> Mg <sub>3</sub> Al <sub>2</sub> -HT     | 43.4                    | 41.1  | 35.1               | 3.047         | 23.125           | 7.5                  | 11.0               | 156.1              | 4.174 | 4.0   |

Table 1. Composition and X-ray diffraction data for the dried and calcined samples.



**Figure 1.** X-ray diffraction patterns of Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT samples dried at 110 °C (**a**), and those calcined at 600 °C (**b**), experimental XRD pattern for NiMg<sub>4</sub>Al<sub>2</sub>-HT sample (gray curves) and calculated XRD patterns (black curves) for models of Ni-Mg-Al oxide nanoparticle with a cubic NaCl-type structure (A) and Ni-Mg-Al oxide nanoparticle, 50% of which are NaCl-like layers and 50% of which are spinel-like layers (B) (**c**), and Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT sample reduced in H<sub>2</sub> at 700 °C (**d**) (1—NiMg<sub>4</sub>Al<sub>2</sub>-HT, 2—Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT, 3—Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT, and 4—Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT).

The XRD patterns of the samples calcined at 600 °C are shown in Figure 1b. All the XRD patterns exhibit reflections, which are characteristic of an oxide with a cubic NaCl-type crystal structure (s.g. Fm3m). Such a crystal structure is typical of periclase MgO (PDF#00-045-0946, a = 4.211 Å) and NiO oxide (PDF#00-047-1049, a = 4.177 Å). The determined crystal lattice parameters and average CSD sizes are listed in Table 1. The lattice parameter of the obtained Ni-Mg-Al oxides decreases with an increase in Ni content. This is related to the enrichment by smaller Ni<sup>2+</sup> ions. Thus, the radius of Ni<sup>2+</sup> ions in octahedral coordination is smaller than that of Mg<sup>2+</sup> ions (0.69 vs. 0.72 Å). The observed intensification of the 111 reflection with an increase in Ni content (Figure 1b) also indicates the enrichment of the mixed oxides by the Ni cations.

All the XRD patterns are accompanied by the presence of an additional diffuse scattering peak at 30–36° near the 111 reflection (Figure 1b). The presence of this diffuse scattering seems to be a consequence of the specific nanostructure of mixed oxides obtained from LDH. Cherepanova et al. [35] carried out a comprehensive study of the structure of Mg-Al mixed oxides obtained by thermal decomposition of Mg-Al LDH and showed that the appearance of the diffuse scattering in this region is caused by the particles nanostructuring. A simulation of XRD patterns for 1D disordered crystals was used and it was shown that the structure of Mg-Al mixed oxides consists of alternating layers of cations in octahedral coordination, which is characteristic of a NaCl-type structure (MgO, NiO), and layers of cations in octahedral and tetrahedral coordination, which are characteristic of the spinel structure (MgAl<sub>2</sub>O<sub>4</sub>).

In this work, for NiMg<sub>4</sub>Al<sub>2</sub>-HT samples calcined at 600 °C, the modeling XRD pattern was performed (Figure 1c). We performed a simulation of XRD patterns using the Debye scattering equation to check the proposed nanostructure models for the Ni-Mg-Al oxides under study. The dimensions of the model nanoparticles were set on the basis of the determined average CSD size ( $d_{XRD}$  = 4 nm). It is known that that after the calcination of Ni-Mg-Al hydrotalcite-like materials, Mg-Ni-O solid solution phases and MgAl<sub>2</sub>O<sub>4</sub> spinel structures are usually formed [27,36]. Formerly, the model Ni-Mg-Al oxide nanoparticle with a cubic NaCl-type structure was considered. Comparison between calculated and experimental XRD patterns showed that this model was not suitable (Figure 1c (curve A)). The calculated XRD profile differs from the experimental one. The experimental XRD pattern shows an additional diffuse peak at 35° near the 111 reflection. At the next stage, the model of the nanostructured particle was considered. The nanostructured particles model was created on the basis of the  $MgAl_2O_4$  spinel structure (s.g. Fd3m). In 111, the layers of the MgO structure with octahedrally coordinated cations were alternated with the layers of the spinel structure with octahedrally and tetrahedrally coordinated cations. The model assumes the statistic distribution of Mg<sup>2+</sup>, Ni<sup>2+</sup> and Al<sup>3+</sup> cations. The occupancies of 16d, 16c and 8a sites were 1, 0.6 and 0.3, respectively. As can be seen in Figure 1c (curve B), the agreement between the experimental and calculated XRD profiles is significantly better. The considered model describes the appearance of additional diffuse scattering causing the abnormal shape of the 111 reflection. The obtained results suggest that the Ni-Mg-Al mixed oxides under study have a specific nanostructure, which is an intermediate between a MgO and spinel structure.

Figure 1d shows the XRD pattern of Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT calcined at 600 °C and then reduced in H<sub>2</sub> at 700 °C. The sample contained a crystalline phase of metallic nickel with the cubic unit cell parameter a = b = c = 3.5271 Å (PDF no. 04-0850, a = b = c = 3.524 Å). The XRD pattern also contained the peak characteristics of an oxide with a cubic NaCl-type structure and the lattice parameter a = b = c = 4.184 Å. The observed ratio of the peak intensities indicates the formation of a mixed oxide. Compared to the initial sample calcined at 600 °C, a significant increase in the lattice parameter, a decrease in the ratio of the peak intensities, and the formation of the Ni<sup>0</sup> crystalline phase was observed, which indicates the release of nickel atoms from the mixed oxide upon reduction with the formation of Ni<sup>0</sup> metal particles. Furthermore, an additional diffuse scattering peak at 30–36° in 20 was retained owing to the mixed oxide particle nanostructure.

According to the low-temperature nitrogen adsorption data, the specific surface area of samples dried at 110 °C ranges within 35.1–52.7 m<sup>2</sup>/g (Table 1). Increasing the heat treatment temperature to 600 °C causes a significant increase in the S<sub>BET</sub> value. All samples are characterized by a relatively high specific surface area (156.1–209.1 m<sup>2</sup>/g) (Table 1). The increase in the specific surface area is explained by the transformation of the crystalline hydrotalcite-type structure into dispersed metal oxides. This process is accompanied by the release of water and CO<sub>2</sub>, which promotes the formation of new pores according to the literature [37]. As the Ni<sup>2+</sup>/Mg<sup>2+</sup> ratio increases, the respective S<sub>BET</sub> value decreases (Table 1), which is similar to the previously reported values for hydrotalcite-derived materi-

als [38,39]. This fact most likely relates to the partial pore blocking with the reconstruction of the material [39].

Thermal analysis of the nickel catalysts dried at 110 °C was performed. The results are shown in Figure S1. During heating from room temperature to 1000 °C, the samples lost 39.2% to 41.6% of their weight (Table S1). All samples were characterized by two temperature ranges of weight loss (Figure S1). According to the literature data, at temperatures below 300 °C, the loss of physically adsorbed and interlayer water occurs; in the temperature range of 300–500 °C, the dehydroxylation of hydroxide layers, and removal of carbonate interlayer anions occur [40,41].

To study the reducibility of the Ni<sub>x</sub>Mg<sub>4-x</sub>Al<sub>2</sub>-HT samples calcined at 600 °C, TPR measurements were carried out. The resulting TPR profiles are shown in Figure S2. During high-temperature reduction, a significant structural rearrangement of the mixed oxide occurs. Typically, NiO is reduced at a temperature of ~330 °C [42,43]. Our samples demonstrated a clear reduction peak in the high temperature region (600–800 °C). According to XRD data, the catalysts formed a mixed oxide under high-temperature synthesis. It is reasonable to assume that the reduction of Ni<sup>2+</sup> from the mixed oxide was impeded due to the strong interaction of Ni<sup>2+</sup> within the Ni-Mg-Al-O support [44,45].

The obtained TPR data allow the conclusion that the temperature of the oxide precursor reduction must be at least 700  $^{\circ}$ C to ensure the formation of the metallic nickel phase.

To study the sample's compositional homogeneity, STEM-HAADF images and EDX elemental mapping patterns were obtained (Figure 2). It appeared that the cations (Ni, Mg, Al) were uniformly distributed throughout the plate; no areas were observed to be enriched with one or another element (Figure 2a,b).



**Figure 2.** HAADF STEM (**a**), EDX elemental mapping (**b**) and HRTEM images (**c**,**d**) of  $Ni_{1.6}Mg_{3.4}Al_2$ -HT calcined at 600 °C.

HRTEM images demonstrating the particle's morphology and microstructure are shown in Figure 2c,d, respectively. It can be seen that the sample consists of particle agglomerates widely varied in size (from 10 nm to several microns). The particles are composed of disordered lamellar crystallites ranging from 5 to 20 nm in size (Figure 2c). The studies of the sample microstructure showed that, apart from the interplanar distances of 2.4 Å (shown by white arrows (Figure 2d)), corresponding to the 111 planes, the distances 2.53–2.58 Å are observed in crystallites, which contradict the cubic nickel oxide structure, and, most likely, correspond to inclusions of a spinel structure (shown by red arrows) (Figure 2d). These distances are observed predominantly on crystallite faces and comply with the distances obtained from the XRD data. It is worth noting that the crystal structure in these areas contains dislocations, which are seen in the HRTEM images as sharp interruptions of the crystal lattice in neighboring planes.

In Figure 3, we can see HRTEM images, the distribution histograms of nickel particles of all the catalysts reduced in H<sub>2</sub> at 700 °C and the microstructure of the Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT and Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT samples. The studies of the sample microstructure showed that the observed crystallites correspond to a metal nickel structure. The nickel particles are evenly distributed over the surface of the catalyst (Figure 3 and Figure S3). In agreement with the HRTEM data, in all the synthesized nickel catalysts reduced at 700 °C (in H<sub>2</sub>), particle size was mainly distributed between 15–20 nm.

According to the literature data, the reaction of ammonia decomposition is significantly affected by the basic properties of the catalyst [46]. It is known that a magnesium oxide additive facilitates an increase in the specific surface area and basicity of the catalyst [42].

All the samples studied are characterized by a profile of temperature-programmed CO<sub>2</sub> desorption with a predominant contribution of the basic sites in the region of 100–350 °C, but for Ni<sub>1</sub>Mg<sub>4</sub>Al<sub>2</sub>O<sub>x</sub>, an additional contribution of the stronger basicity sites is observed in the region of 300–600 °C (Figure 4 and Table 2). At the same time, the density of the basic sites remains approximately at the same level for all the samples. Hence, we considered the correlation between the molar ratios of Mg/Ni and Mg/Al and the rate of H<sub>2</sub> formation, assuming that in our case, with an increase in the magnesium content, an increase in basicity also occurred. As can be seen (in Figures S4 and S5), the higher the basicity of the support (Mg/Ni, Mg/Al molar ratios), the lower the activity of the catalyst (H<sub>2</sub> rate). On the other hand, an increase in the molar fraction of Ni relative to the sum of Al and Mg clearly correlates with an increase in the activity of the catalyst in the decomposition of ammonia (Figure S6).

Figure 5 shows the temperature dependences of the ammonia decomposition performance of Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts reduced in H<sub>2</sub> at 700 °C) with different Ni/Mg molar ratios. For all catalysts, ammonia conversion increases with increasing temperature owing to endothermic character of the reaction [46]. At 500 °C, ammonia conversion increases proportionally to the increase in the Ni/Mg ratio in the catalysts: NiMg<sub>4</sub>Al<sub>2</sub>-HT < Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT < Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT < Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT (Figure 5, Table 3). This is most likely associated with an increase in the active nickel surface area. At GHSV 72,000 mL/(h·g<sub>cat</sub>) and 500 °C, the Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT catalyst possessing the highest nickel content demonstrates a NH<sub>3</sub> conversion of 29.6%, which corresponds to the H<sub>2</sub> formation rate of 23.8 mmol/(g<sub>cat</sub>·min) (Table 3).

In the temperature range of 550–700 °C, the Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT catalyst demonstrated the highest activity (Figure 5). The maximum catalytic characteristics of this catalyst were observed at a reaction temperature of 700 °C, with NH<sub>3</sub> conversion being 99.1%, and H<sub>2</sub> productivity being 82.9 mmol/(g<sub>cat</sub>·min). The other catalysts showed similar catalytic properties in this temperature range. It can be assumed that the active component, to a greater extent than the carrier, determines the activity of the catalyst. In agreement with the TEM data (Figure 3), for all reduced Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts the Ni particle sizes are very close. Therefore, we believe that the nickel content makes the main contribution to the activity of the catalyst in ammonia decomposition.



**Figure 3.** HRTEM images and distribution histograms of nickel particles of the reduced (H<sub>2</sub>, 700 °C) catalysts: (**a**) NiMg<sub>4</sub>Al<sub>2</sub>-HT, (**b**) Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT, (**c**) Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT, and (**d**) Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT).



Figure 4. CO<sub>2</sub>-TPD profiles of calcined Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts (600 °C).

Table 2. The basicity of  $Ni_xMg_yAl_2$ -HT catalysts determined by the method of temperature-programmed  $CO_2$  desorption.

| Catalynt  | T °C                                      | The Amount of CO <sub>2</sub> Desorbed |     |  |  |
|---|---|--|-----|--|--|
| Catalyst  | $I_{Max}$ , C                             | I <sub>Max</sub> , C μmol/g            |     |  |  |
| Ni <sub>1</sub> Mg <sub>4</sub> Al <sub>2</sub> -HT     | ~163, with the shoulder<br>at more high T | 183                                    | 0.9 |  |  |
| Ni <sub>1.3</sub> Mg <sub>3.7</sub> Al <sub>2</sub> -HT | 169                                       | 143                                    | 0.8 |  |  |
| Ni <sub>1.6</sub> Mg <sub>3.4</sub> Al <sub>2</sub> -HT | 169                                       | 148                                    | 0.8 |  |  |
| Ni2Mg4Al2-HT  | 166                                       | 133                                    | 0.9 |  |  |



**Figure 5.** The influence of the reaction temperature on NH<sub>3</sub> conversion over  $Ni_xMg_yAl_2$ -HT catalysts (700 °C, H<sub>2</sub>) (GHSV 72,000 h<sup>-1</sup>).

| Catalyst   | Ni Content<br>wt.% | GHSV,<br>mL/(g <sub>cat</sub> ·h) | <b>T,</b> <sup>°</sup> C | Conversion,<br>% | H <sub>2</sub> Rate,<br>mmol/(g <sub>cat</sub> ·min) | T <sub>50</sub> ,<br>°C | Ref.       |
|--|--------------------|-----------------------------------|--------------------------|------------------|--|-------------------------|------------|
| NiMg <sub>4</sub> Al <sub>2</sub> -HT                                | 16.9               | 72,000                            | 500                      | 20.7             | 16.6   | 608                     | This study |
| Ni <sub>1.3</sub> Mg <sub>3.7</sub> Al <sub>2</sub> -HT              | 21.5               | 72,000                            | 500                      | 25.9             | 20.8   | 570                     | This study |
| Ni <sub>1.6</sub> Mg <sub>3.4</sub> Al <sub>2</sub> -HT              | 25.3               | 72,000                            | 500                      | 26.2             | 21.1   | 600                     | This study |
| Ni2Mg3Al2-HT   | 30.7               | 72,000                            | 500                      | 29.6             | 23.8   | 590                     | This study |
| NIAP-13-02   | 22.5               | 72,000                            | 500                      | 15.8             | 12.7   | 616                     | This study |
| Ni <sub>0.6</sub> Al <sub>0.9</sub> O <sub>n</sub>                   | 40.5               | 30,000                            | 500                      | 31.0             | 10.4   | 530                     | [42]       |
| Ni <sub>0.6</sub> Mg <sub>0.3</sub> Al <sub>0.6</sub> O <sub>n</sub> | 40.1               | 30,000                            | 500                      | 42.0             | 14.1   | 508                     | [42]       |
| 20Ni/La-MgO  | 20                 | 22,000                            | 500                      | 84.0             | 21.0   | 449                     | [47]       |
| Ni/C-LDHs-ST   | 23.6               | 30,000                            | 500                      | 20.4             | 6.8  | 549                     | [48]       |
| Ni_MgAl  | 15.0               | 60,000                            | 500                      | 17.0             | 11.4   | 582                     | [49]       |

**Table 3.** Comparison of the  $NH_3$  decomposition activity of nickel based catalysts (700 °C,  $H_2$ ).

The catalytic properties of the synthesized samples were compared with those of industrial catalyst NIAP-13-02 (Figure 5, Table 3). The Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts showed superior activity over the industrial catalyst. NH<sub>3</sub> conversion over Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT at 500 °C exceeded the respective value for NIAP-13-02 by ~40%.

We tested our samples in NH<sub>3</sub> decomposition process at 500 °C, because the literature data report highly active nickel-based catalysts that perform almost complete ammonia decomposition exactly at this temperature [49]. As is seen in Table 3 and Table S2, the reduced Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT systems exceed in catalytic performance respective to the analogues presented in the literature, which can be most likely related to the improved structural characteristics (Table 1). The insignificant increase in the activity of the Ni<sub>1.3</sub> g<sub>3.7</sub>Al<sub>2</sub>-HT catalyst compared to that of other samples at 700 °C can be explained by the slightly smaller nickel particles (Figure 3).

#### 3. Experimental

#### 3.1. Synthesis of Nickel Catalysts

Ni-, Mg- and Al-based samples were synthesized by coprecipitation in a solution containing appropriate quantities of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O; a solution of 1 M NaOH and 0.5 M Na<sub>2</sub>CO<sub>3</sub> (OOO "VEKTON", Russia, Saint Petersburg) was added slowly under vigorous stirring. The mixed solution was maintained at pH 10. The obtained suspension was stirred for 18 h, filtered and washed several times with deionized water until the washings were neutral. The solid was dried at room temperature and then at 110 °C for 10 h. The resulting hydroxides were calcined at 600 °C for 5 h. The obtained samples were synthesized with the atomic ratio (Ni<sup>2+</sup> + Mg<sup>2+</sup>)/Al<sup>3+</sup> = 2.5, and the Ni and Mg contents: were as follows: Ni<sub>x</sub>Mg<sub>4-x</sub>Al<sub>2</sub>-HT with x = 1, 1.3, 1.6, and 2).

### 3.2. Physicochemical Methods for the Catalysts Characterization

The BET surface area of the support, and of the as-prepared and used catalysts, was determined from the complete nitrogen adsorption isotherms at -196 °C (ASAP 2400 instrument) (Micromeritics, Norcross, GA, USA).

Powder X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer (Bruker, Karsruhe, Germany) (Cu K<sub> $\alpha$ </sub> radiation,  $\lambda = 0.15418$  nm) equipped with a LynxEye position-sensitive detector. The measurements were performed in the 20 range of 10°–75° with a step of 0.05° and a collection time of 3 s. The average sizes of the coherently scattering domains (CSD), d<sub>XRD</sub>, were estimated by the Scherrer equation.

For elemental analysis, catalyst samples were examined by X-ray fluorescence spectroscopy. The secondary spectrum was recorded on an ARL Perform'X X-ray fluorescence spectrometer (Thermo Scientific<sup>TM</sup>, Waltham, MA, USA). The spectrum was processed and the content of elements was calculated using the UniQuant Software for Standardless XRF Analysis (Thermo Scientific<sup>TM</sup>, Waltham, MA, USA). An algorithm based on the Debye scattering equation (DSE) was used for the direct simulation of XRD patterns from model nanostructured particles. The Debye function analysis (DFA) method is widely used for studying nanocrystals because of the possibilities to simulate XRD patterns for particles with a high-dispersion, non-crystalline or highly defective structure [50–54]. The DSE is simply expressed as

$$I(Q) = P(Q)\sum_{i}\sum_{j}f_{i}(Q)f_{j}(Q)\frac{\sin(Qr_{ij})}{Qr_{ij}}$$
(1)

where  $Q = 4\pi \cdot \sin(\theta) / \lambda$  is a scattering vector value; P(Q) is the correction functions;  $f_i(Q)$  and  $f_j(Q)$  are atomic form factors; and  $r_{ij}$  is the interatomic distances.

The DIANNA software [55,56] was used for the generation of atomistic models of nanostructured particles and simulation of corresponding XRD patterns.

The thermal decomposition of the samples was evaluated by TGA and DTA analyses carried out in Netzsch TT-209 apparatuses (Netzsch, Selb, Germany). in the temperature range from 20 to 1000 °C at a heating rate of 10 °C/min in Ar (30 mL/min). The sample weight was 45 mg, and the error in the weight loss measurements was  $\pm 0.1\%$ .

Thermal analysis (TPR) was conducted on TG209 F1 Libra Thermo microbalance equipment (Netzsch, Selb, Germany). The feed gas He + 6 vol.% H<sub>2</sub> flowed at the rate 70 mL/min. The temperature was raised linearly from 30 to 800 °C at a rate of 10 °C/min. Gas phase composition over the sample was monitored by the QMS 200 gas analyzer (Stanford Research Systems, Sunnyvale, CA, USA).

The measurements of CO<sub>2</sub> adsorption–desorption were made on a precision chemisorption analyzer, AutoChem-2920 Micromeritics (Micromeritics, Norcross, GA, USA). Before the temperature-programmed desorption (TPD) experiment, the sample was heated in a helium flow to 600 °C for 60 min, and then the sample was cooled in a helium flow to a temperature of 100 °C. CO<sub>2</sub> adsorption was carried out at 100 °C for 60 min, and then it was purged with helium for 60 min at 100 °C to remove physically adsorbed CO<sub>2</sub>. The feed gas He + 10 vol.% CO<sub>2</sub> flowed at the rate 30 cm<sup>3</sup>/min. The temperature was raised linearly from 100 to 600 °C at a rate of 10 °C/min.

For shooting in the TEM and STEM modes, a ThemisZ two-corrector transmission electron microscope (Thermo Scientific<sup>™</sup>, Waltham, MA, USA) with an accelerating voltage of 200 kV and a limiting resolution of 0.07 nm (TEM) and 0.06 nm (SEM) was used. Micrographs were recorded using a Ceta 16 CCD matrix (Thermo Scientific<sup>™</sup>, Waltham, MA, USA).

The catalyst activity in the ammonia decomposition was studied in a fixed-bed flowtype reactor at an atmospheric pressure in the temperature range 500–700 °C. A commercial catalyst for the steam reforming of methane, NIAP-13-02 (22.5 wt.% Ni/Al<sub>2</sub>O<sub>3</sub>) ("NIAP-Katalizator" Ltd., Novomoskovsk, Russia), was used for the comparison. The weight of the loaded catalysts was approximately 0.02 g. Before the experiment, all samples were reduced in a H<sub>2</sub> flow at 700 °C for 4 h. Pure NH<sub>3</sub> was fed to the reactor at a rate of 60–100 mL/min. The gas mixture at the reactor outlet was analyzed using a Tsvet-500M chromatograph (Tsvet, Krasnogorsk, Russia) with a thermal conductivity detector, and hydrogen as a carrier gas. A column, 1.5 m long, was packed with the HayeSep C sorbent (Hayes Separation, Bandera, TX, USA), which allows one to separate NH<sub>3</sub> and N<sub>2</sub>. The chromatography conditions were as follows: the carrier gas was hydrogen, the flow rate was 60 mL/min, the pressure was 1 atm, the bridge voltage was 4 V, and the column temperature was 70 °C. Based on the data obtained, ammonia conversion and specific catalytic activity (W<sub>sp</sub>, in mmol/(g<sub>cat</sub>·min)) were calculated.

### 4. Conclusions

Thus, LDH-based  $Ni_xMg_yAl_2$ -HT catalysts with a constant ratio (Ni + Mg)/Al = 2.5 and varying Ni/Mg ratios were synthesized by the coprecipitation method. The physic-ochemical and catalytic properties of the obtained catalysts were studied. The XRD data

proved that the dried samples were layered double hydroxides. During the heat treatment at 600 °C, the formation of Ni-Mg-Al mixed oxides of a specific nanostructure, which is an intermediate between a NaCl and spinel structure, occurred. The lattice parameter (a = 4.174–4.181 Å) in the samples increased with the decreasing Ni/Mg ratio. The synthesized catalysts possessed a high specific surface area (156.1–209.1 m<sup>2</sup>/g) which also increased with the decreasing Ni/Mg ratio. According to the EDX data, the catalysts had a uniform distribution of particles in the volume. In agreement with the HRTEM data, in all the synthesized nickel catalysts reduced at 700 °C (in H<sub>2</sub>), particle size was mainly distributed between 15–20 nm. The results of the basicity determination by the method of thermal desorption of CO<sub>2</sub> showed that the strength of the basic support sites was almost the same.

The catalysts were highly active in the process of ammonia decomposition. At a process temperature of 500 °C, the ammonia conversion on the catalysts increased with the increasing Ni/Mg ratio. The Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT catalyst showed a H<sub>2</sub> productivity of 23.8 mmol/(g<sub>cat</sub>·min). Clearly, the catalysts based on layered double hydroxides synthesized by the described method are quite competitive with world analogues. It was found, that the nickel content makes the main contribution to the activity of the catalyst in ammonia decomposition.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal13040678/s1, Table S1. Thermoanalytical data for nickel based catalysts; Figure S1. DTA and DTG profile of the samples; Figure S2. Time dependence of H<sub>2</sub> MS-signal and temperature for Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT samples calcined at 600 °C (1-NiMg<sub>4</sub>Al<sub>2</sub>-HT, 2-Ni<sub>1.3</sub>Mg<sub>3.7</sub>Al<sub>2</sub>-HT, 3-Ni<sub>1.6</sub>Mg<sub>3.4</sub>Al<sub>2</sub>-HT, 4-Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT); Figure S3. HAADF STEM (left) and EDX elemental mapping (right) of reduced Ni<sub>2</sub>Mg<sub>3</sub>Al<sub>2</sub>-HT sample (700 °C, H<sub>2</sub>); Table S2. Comparison of the ammonia decomposition activity of nickel based catalysts; Figure S4. Correlation between the Mg/Ni molar ratio and the H<sub>2</sub> formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min); Figure S6. Correlation between the Mg/Al molar ratio and the H<sub>2</sub> formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over Ni<sub>x</sub>Mg<sub>y</sub>Al<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min); Figure S6. Correlation between the Ni/(Mg + Al) molar ratio and the H2 formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over NixMgyAl<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min); Figure S6. Correlation between the Ni/(Mg + Al) molar ratio and the H2 formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over NixMgyAl<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min); Figure S6. Correlation between the Ni/(Mg + Al) molar ratio and the H2 formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over NixMgyAl<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min); Figure S6. Correlation between the Ni/(Mg + Al) molar ratio and the H2 formation rates (mmol H<sub>2</sub>/(g<sub>cat</sub>·min) for NH<sub>3</sub> conversion over NixMgyAl<sub>2</sub>-HT catalysts (700 °C, H<sub>2</sub>) (flow rate 60 mL/min) [1,12,47,48,57–61].

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